

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Ho-Hin Kweon, et al.

Continuation of Serial No.: 09/248,202

For: **POSITIVE ACTIVE MATERIAL FOR  
RECHARGEABLE LITHIUM BATTERY AND  
METHOD OF PREPARING SAME**

PRELIMINARY AMENDMENT

Assistant Commissioner for Patents  
Washington, D.C. 20231

Dear Sir:

Submitted herewith is a continuation application, namely a copy of the original application as filed, Declaration and drawings as originally filed.

Also submitted herewith is a substitute specification with claims for use in examination of the continuation application. Also included is a red-lined copy of the substitute specification and claims. Applicant states that no new matter has been added. Additionally, submitted herewith are new drawings for use with the substitute specification to replace the original drawings.

Respectfully submitted,

BLAKELY, SOKOLOFF, TAYLOR & ZAFMAN

Dated: 11/7/02

By: 

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# **SUBSTITUTE SPECIFICATION**

10041921.010702

**POSITIVE ACTIVE MATERIAL FOR RECHARGEABLE LITHIUM BATTERY  
AND METHOD OF PREPARING SAME**

**CROSS REFERENCE TO RELATED APPLICATION**

5 This application is a continuation application of pending prior United States Patent Application Serial No. 09/248,202, filed on February 10, 1999, which is incorporated by reference herein in its entirety. In addition, Korean Patent Application Nos. 98-3755, 98-12005, and 98-42956 filed on February 10, April 6, and October 14, 1998, and entitled: "Active material for positive electrode used in the lithium secondary battery and method of manufacturing the same," is incorporated by reference herein in its entirety.

**BACKGROUND OF THE INVENTION**

**(a) Field of the Invention**

10 The present invention relates to a positive active material for a rechargeable lithium battery and a method of preparing the same, and more particularly, to a positive active material for a rechargeable lithium battery and a method of preparing the same in which the positive active material exhibits improved structural and thermal stability.

**(b) Description of the Related Art**

15 20 The use of portable electronic instruments is increasing as electronic equipment gets smaller and lighter due to developments in high-tech electronic industries. Studies on rechargeable lithium batteries are actively being pursued in accordance with the increased need for a battery having a high

energy density for use as a power source in these portable electronic instruments.

Rechargeable lithium batteries use material into or from which lithium ions are reversibly intercalated or deintercalated as negative and positive active materials. For an electrolyte, an organic solvent or polymer is used. Rechargeable lithium batteries produce electrical energy from changes of chemical potentials of the active material during the intercalation and deintercalation reactions of lithium ions.

For the negative active material in a rechargeable lithium battery, metallic lithium was used in the early period of development. However, the lithium negative electrode degrades due to a chemical reaction with the electrolyte. Lithium dissolved in an electrolyte as lithium ions upon discharging is deposited as lithium metal on the negative electrode upon charging. When charge-discharge cycles are repeated, lithium is deposited in the form of dendrites which are more reactive toward the electrolyte due to an enhanced surface area, and they may also induce a short circuit between the negative and positive active materials and even cause an explosion of the battery in the worse case. Such problems have been addressed by replacing lithium metal with carbon-based materials such as an amorphous or crystalline carbon. The carbon-based materials reversibly accept and donate significant amounts of lithium without affecting their mechanical and electrical properties, and the chemical potential of lithiated carbon-based material is almost identical to that of lithium metal.

For the positive active material in the rechargeable lithium battery, a

metal chalcogenide compound into or from which lithium ions are intercalated or deintercalated is used. Typical examples include  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNiO}_2$ ,  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  ( $0 < x < 1$ ), or  $\text{LiMnO}_2$ . Mn-based active materials such as  $\text{LiMn}_2\text{O}_4$  or  $\text{LiMnO}_2$  are the easiest to prepare and they are less expensive and much more environmentally friendly than the other materials, but they have significantly smaller capacities than the other materials.  $\text{LiCoO}_2$  exhibits good electrical conductivity of  $10^{-2}$  to 1 S/cm at ambient temperatures, as well as high cell voltage and good electrochemical properties. Therefore, it is widely used in commercially available rechargeable lithium batteries, although the cobalt-based active material is relatively more expensive than the other materials.  $\text{LiNiO}_2$  has an advantage of having the highest specific capacity of all, but it is relatively more difficult to synthesize in the desired quality level and is the least stable of all.

These composite metal oxides are manufactured by a solid-phase method. The solid-phase method involves mixing solid raw material powders and sintering the mixture. For example, Japanese Patent publication No. Hei 8-153513 discloses a method in which  $\text{Ni(OH)}_2$  is mixed with  $\text{Co(OH)}_2$  or mixed hydroxides of Ni and Co are heat-treated, ground, and then sieved to produce  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  ( $0 < x < 1$ ). In another method, a reactant mixture of  $\text{LiOH}$ , Ni oxide and Co oxide is initially heated at 400 to 580°C, and then the heated reactant is heated again at 600 to 780°C to produce a crystalline active material.

Another way to produce such composite metal oxides is disclosed in Japanese Patent Laid open Hei. 9-55210 (Sony). In this method, a Ni-based material is coated with a metal alkoxide to prepare a positive active material.

The metal alkoxide includes Co, Al or Mn. However, the metal coatings in the Ni-based material did not show improvements in the cell performance, e.g. capacity and voltage.

In addition, U.S. Patent No. 5,705,291 (Bell Communications Research, Inc.) discloses that  $\text{LiMn}_2\text{O}_4$  is mixed with aluminum oxide and briefly heated to obtain an active material with improved behavior. However, this material did not provide with a sufficient improvement in cell performances to satisfy commercial needs.

Therefore, there is sufficient need to develop positive active materials with improved structural and thermal stability, capacity, and cycle life.

### **SUMMARY OF THE INVENTION**

It is an object of the present invention to provide active material for a rechargeable lithium battery with improved structural and thermal stability, capacity and cycle life.

It is another object of the present invention to provide a method of preparing the positive active material for a rechargeable lithium battery.

To achieve the above objects, the present invention provides a positive active material for a rechargeable lithium battery including a core comprising at least one compound represented by Formula 1 and a protective active metal oxide shell formed on the core, the active metal oxide being capable of stabilizing a structure of the active material:

Formula 1



where  $0 \leq x \leq 0.3$ , and  $0 \leq y \leq 0.01$ ;

A is an element selected from the group consisting of Co and Mn;

B is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al; and

C is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al.

The positive active material is obtained from a process of preparing crystalline powder or semi-crystalline powder represented by Formula 1, coating the crystalline or semi-crystalline powder with a metal alkoxide suspension, and heat-treating the coated powder.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

Further objects and other advantages of the present invention will become apparent from the following description in conjunction with the attached drawings, in which:

FIGs. 1A and 1B are scanning electronic microscope (SEM) pictures of a positive active material prepared according to Example 1 of the present invention;

FIGs. 2A and 2B are SEM pictures of a positive active material prepared according to Comparative Example 1;

FIG. 3 is a graph illustrating XRD patterns of positive active materials prepared according to Example 2 (b) of the present invention, Comparative Example 2 (c), and semi-crystalline  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  (a);

FIG. 4 is a graph illustrating cycle-life characteristics of cells prepared

according to Example 1 (a) and Example 3 (b) of the present invention, and Comparative Example 1 (c);

FIGs. 5A and 5B are SEM pictures of positive active materials prepared according to Example 5 of the present invention and Comparative Example 3, respectively;

FIG. 6 is a graph illustrating XRD patterns of positive active materials prepared according to Example 5 (A) of the present invention and Comparative Example 3 (B) and Comparative Examples 4 (C);

FIG. 7 is a graph illustrating cycle-life characteristics of cells prepared according to Example 5 (a) of the present invention and Comparative Example 3 (b);

FIG. 8 is a graph illustrating differential scanning calorimetry (DSC) analysis results of positive electrodes prepared according to Example 9 (b) of the present invention and Comparative Example 5 (a);

FIG. 9 is a graph illustrating cycle-life characteristics of cells prepared according to Example 9 (a) of the present invention and Comparative Example 5 (b) for charge and discharge in the voltage range of 4.1 to 2.75V;

FIG. 10 is a graph illustrating cycle-life characteristics of cells prepared according to Example 9 (a) of the present invention and Comparative Example 5 (b) for charge and discharge in the voltage range of 4.2 to 2.75V;

FIG. 11 is a graph illustrating cycle-life characteristics of cells prepared according to Example 9 (a) of the present invention and Comparative Example 5 (b) for charge and discharge in the voltage range of 4.3 to 2.75V;

FIG. 12 is a graph illustrating XRD patterns of positive active materials of



Comparative Example 5 (a) before charging, and Example 10 (b) of the present invention after charging at 4.2V and Comparative Example 5 (c) after 1 cycle charging at 4.2V;

FIG. 13 is a graph illustrating DSC analysis results of positive electrodes after charging at 4.2V, prepared according to Example 10 (b) of the present invention and Comparative Example 5 (a);

FIG. 14 is a graph illustrating DSC analysis results of positive electrodes after charging at 4.1V, prepared according to Example 10 (b) of the present invention and Comparative Example 5 (a);

FIG. 15 is a graph illustrating DSC analysis results of positive electrodes after charging at 4.1V, prepared according to Example 11 (b) of the present invention and Comparative Example 6 (a);

FIG. 16 is a graph illustrating DSC analysis results of positive electrodes after charging at 4.3V, prepared according to Example 12 (b) of the present invention and Comparative Example 7 (a);

FIG. 17 is a graph illustrating DSC analysis results of positive electrodes after charging at 4.3V, prepared according to Example 13 (b) of the present invention and Comparative Example 8 (a);

FIG. 18 is a transmission electronic microscopy (TEM) picture of a positive active material prepared according to Example 14 of the present invention;

FIG. 19 is a TEM picture of a positive active material prepared according to Example 15 of the present invention;

FIG. 20 is a graph illustrating a cycle life characteristics of cells prepared

according to Example 16 (a) of the present invention and Comparative Example 10 (b);

FIG. 21 is a graph illustrating charge-discharge characteristics of a cell prepared according to Example 17 of the present invention;

FIG. 22 is a graph illustrating charge-discharge characteristics of a cell with the positive active material prepared according to Comparative example 11.

FIG. 23 is a graph illustrating cycle life characteristics of cells prepared according to Example 18 (open circles) of the present invention and Comparative Example 12 (filled circles);

FIG. 24 is a graph illustrating the charge and discharge characteristics of the positive active materials according to Example 19 (B) of the present invention and Comparative example 13 (A); and

FIG. 25 is a graph illustrating XRD results of a synthesized  $\text{Al}_2\text{O}_3$  (B) and a commercial  $\text{Al}_2\text{O}_3$  (A);

FIG. 26 is a graph illustrating the charge and discharge characteristics of the coin-type half-cells containing  $\text{LiCoO}_2$  (A) and  $\text{LiCoO}_2$  coated with  $\text{Al}_2\text{O}_3$  (B) and  $\text{LiCoO}_2$  coated with a commercial  $\text{Al}_2\text{O}_3$  (C);

FIG. 27 is a SEM picture of a positive active material according to Example 21 of the present invention;

FIG. 28 is a SEM picture of a positive active material according to Comparative example 15;

FIG. 29 is a graph illustrating an EDX result of a positive active material according to Example 21 of the present invention; and

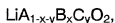
FIG. 30 is a graph illustrating an EDX result of a positive active material

according to Comparative example 15.

### **DETAILED DESCRIPTION OF THE INVENTION**

A positive active material of the present invention includes a core including at least one compound represented by Formula 1 and a protective active metal oxide shell formed on the core:

Formula 1



where  $0 \leq x \leq 0.3$ , and  $0 \leq y \leq 0.01$ ;

A is an element selected from the group consisting of Co and Mn;

B is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al; and

C is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al.

The core preferably includes  $\text{LiCoO}_2$ , and a metal in the active metal oxide includes Mg, Al, Co, K, Na or Ca, and preferably Al. Thus, the preferred metal oxide is active  $\text{Al}_2\text{O}_3$ . The active metal oxide has an amorphous phase. The metal oxide is capable of stabilizing the active material.

A method of preparing the positive active material will be illustrated in more detail.

An A-metal salt is mixed with a B-metal salt in an equivalence ratio of between 70:30 and 100:0. Alternatively, a trace amount of a C-metal salt may be added to the mixture. If the B-metal salt is present over 30% of the sum of A- and B-metal salts, intercalation and deintercalation reactions of lithium ions

do not proceed without changes in a crystalline structure of the resulting positive active material.

The mixing procedure is preferably performed by dispersing the A-, B- and C-metal salts in a suitable solvent and milling the resulting suspension by using an attritor. Although the solvent may be any solvent in which the A-, B- and C-metal salts are not soluble, preferable examples include water, an alcohol or acetone. Here, the milling is performed at a sufficiently high rate for a sufficient period of time to allow uniform mixing, for example, 400 to 500 rpm for about 1 hour.

For example, a nickel salt such as nickel hydroxide, nickel nitrate, or nickel acetate may be used for the A-metal salt; for the B-metal salt, a cobalt salt such as cobalt hydroxide, cobalt nitrate or cobalt carbonate may be used; and for the C-metal salt, aluminum hydroxide or strontium hydroxide may be used.

The resulting suspension is dried in a drying furnace at about 120 °C for 24 hours and the dried material is ground to prepare an  $A_{1-x-y}B_xC_y(OH)_2$  ( $0 \leq x \leq 0.3$ ,  $0 \leq y \leq 0.01$ ) powder. A lithium salt is added to the produced powder in a desired equivalence ratio and mechanically mixed. For example, the mixture of the lithium salt and  $A_{1-x-y}B_xC_y(OH)_2$  is produced by mixing them in a mortar or grinder.

For the lithium salt, although any one of many simple lithium salts that react with  $A_{1-x-y}B_xC_y(OH)_2$  may be used, it is preferable to use lithium nitrate, lithium acetate or lithium hydroxide. In order to facilitate the reaction between

the lithium salt and  $A_{1-x-y}B_xC_y(OH)_2$ , it is preferable that a suitable solvent such as ethanol, methanol, water or acetone is added, and then the mixture is mixed well by grinding in a mortar until excess liquid solvent disappears from the mixture.

The mixture of the lithium salt and  $A_{1-x-y}B_xC_y(OH)_2$  is heat-treated at a temperature between 400 and 600 °C, thereby producing a crystalline or semi-crystalline, positive active material precursor  $LiA_{1-x-y}B_xC_yO_2$  powder.

Alternatively, the mixture of the lithium salt and  $A_{1-x-y}B_xC_y(OH)_2$  is heat-treated for 1 to 5 hours at a temperature between 400 and 550 °C (first heat-treatment), and the resulting material is again heat-treated for 10 to 15 hours at a temperature between 700 and 900 °C (second heat-treatment), thereby producing a crystalline or a semi-crystalline positive active material precursor  $LiA_{1-x-y}B_xC_yO_2$  powder. If the first heat-treatment temperature is below 400 °C, the metal salts do not react completely with the lithium salts, and if the second heat-treatment temperature is below 700 °C, it is difficult to form the crystalline or the semi-crystalline material of Formula 1. The first and second heat-treatments are performed by increasing the temperature at a rate of 1 to 5 °C /min in a stream of air. The mixture is cooled slowly after turning off the heating source. Preferably, the  $LiA_{1-x-y}B_xC_yO_2$  powder is then reground to distribute the lithium salts uniformly.

Subsequently, the crystalline or semi-crystalline  $LiA_{1-x-y}B_xC_yO_2$  powder is coated with a metal alkoxide suspension. The coating process may be performed by dip-coating or by using any other general-purpose coating

technique. Alternatively, the coating may also be achieved by a sputtering method, a chemical vapor deposition (CVD) method. Any other coating techniques, if available and applicable, may be as effective as the methods described herein, but it is preferable to use a dip-coating method using a metal alkoxide suspension since it is simple to use and economical.

The metal alkoxide suspension is prepared by mixing the metal or metal alkoxide powder with an alcohol at 1 to 10% by weight of the alcohol, preferably followed by refluxing the mixture. The metal of the metal alkoxide may be Mg, Al, Co, K, Na or Ca, preferably Al, and the alcohol may be methanol, ethanol or isopropanol. For the dip-coating process, if the concentration of the metal is less than 1% by weight, advantageous effects of coating the  $\text{LiA}_{1-x-y}\text{B}_x\text{C}_y\text{O}_2$  powder with the metal alkoxide suspension are not sufficient, while if the concentration of the metal exceeds 10% by weight, the coating layer formed by the metal alkoxide suspension on the powder becomes too thick.

After dip-coating the crystalline or semi-crystalline powder with the alkoxide suspension, the wet powder is dried in an oven at 120°C for about 5 hours. This drying step is performed to distribute lithium salt uniformly in the powder. The dried crystalline  $\text{LiA}_{1-x-y}\text{B}_x\text{C}_y\text{O}_2$  powder with coating layer is heat-treated for 8 to 15 hours at a temperature between 400 and 900°C. In the case where the powder is crystalline, it is preferable that the heat-treating temperature is set between 400 and 600°C, whereas the preferable temperature is between 700 and 900°C in the case where the powder is semi-crystalline.

By the heat-treating process, the metal alkoxide suspension is

converted to metal oxide, and the semi-crystalline  $\text{LiA}_{1-x-y}\text{B}_x\text{C}_y\text{O}_2$  powder is converted to a crystalline powder, resulting in the production of positive active material of Formula 1 in which metal oxide is coated on a surface of a crystalline  $\text{LiA}_{1-x-y}\text{B}_x\text{C}_y\text{O}_2$  powder. The metal oxide formed on the surface of the active material can be either a composite metal oxide obtained from at least one of the A-, B- or C- metals and the metal alkoxide, or a metal oxide obtained from only the metal alkoxide. For example, by heat-treating  $\text{LiCoO}_2$  coated with aluminum alkoxide, a positive active material of a composite metal oxide of cobalt and aluminum, and/or a positive active material with a surface on which aluminum oxide is coated, can be obtained. To produce a more uniform crystalline active material, it is preferable to dry in air or oxygen by blowing it thereon during the heat-treating process. If the heat-treating temperature is below  $400^\circ\text{C}$ , since the coated metal alkoxide suspension does not become crystallized, the resulting active material does not give good performance in a battery since the movement of lithium ions therein is hindered.

The resulting positive active material prepared by the process described above is made of agglomerated minute particles, the particle size being between 0.1 and  $100\mu\text{m}$ .

The following examples further illustrate the present invention.

(Example 1)

$\text{Ni}(\text{OH})_2$  powder and  $\text{Co}(\text{OH})_2$  powder were mixed in an equivalence ratio of 0.8:0.2 and dispersed in water, and the resulting material was mixed and milled by using an attritor for 60 minutes at 450 rpm. The resulting mixture was dried in a drying oven at  $120^\circ\text{C}$  for about 24 hours, and the dried mixture

having a composition of  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$  was evenly ground. To this powder, a stoichiometric amount of  $\text{LiOH}$  was added, followed by grinding the resultant powder mixture in a mortar to achieve an even blend.

The resultant powder mixture was heat-treated at  $500^\circ\text{C}$  for about 5 hours to obtain a semi-crystalline powder of  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ . The semi-crystalline  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder was then dip-coated with a  $\text{Mg}$ -methoxide suspension. The  $\text{Mg}$ -methoxide suspension was prepared by refluxing  $\text{Mg}$  powder of 4% by weight of methanol. The coated semi-crystalline powder was remixed at a high temperature in a stream of dry air to distribute lithium salt uniformly. The resulting material was then heat-treated for 12 hours at  $750^\circ\text{C}$  in a stream of dry air to obtain a coated crystalline positive active material.

The positive active material, a conductive agent (carbon), a binder (polyvinylidene fluoride) and a solvent ( $\text{N}$ -methyl pyrrolidone) were mixed to prepare a positive active material slurry. The slurry was then cast into a tape on an  $\text{Al}$  foil current collector to manufacture a positive electrode. Using this positive electrode, a  $\text{Li}$ -metal counter electrode, a sheet of microporous polypropylene separator, and an electrolyte solution of  $1\text{M LiPF}_6$  in a 1:1 volume mixture of ethylene carbonate ( $\text{EC}$ ) and dimethyl carbonate ( $\text{DMC}$ ), a coin-type half-cell was fabricated.

#### (Example 2)

A coin-type half-cell was fabricated by the same procedure as in Example 1, except that acetone was added to the mixture of the lithium salt and  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$  in order to facilitate the reaction between  $\text{LiOH}$  and  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$ , and mortar/grinder mixing was performed until liquid acetone



disappeared from the mixture, instead of dry grinding as in Example 1.

(Example 3)

A coin-type half-cell was fabricated by the same procedure in Example 1, except that a mixture of lithium salt and  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$  was heat-treated for about five hours at  $600^\circ\text{C}$  instead of  $500^\circ\text{C}$  as in Example 1, to produce a semi-crystalline  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder.

(Example 4)

A coin-type half-cell was fabricated by the same procedure in Example 2, except that a mixture of lithium salt and  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$  was heat-treated for about five hours at  $600^\circ\text{C}$ , to produce a semi-crystalline  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder.

(Example 5)

$\text{Ni}(\text{OH})_2$  and  $\text{Co}(\text{OH})_2$  were mixed in an equivalence ratio of 0.8:0.2 and dispersed in water. The resulting mixture was mixed well by milling with an attritor for about 60 minutes at 450 rpm. The mixed powder was dried in water in a drying oven at  $120^\circ\text{C}$  for about 24 hours and the resulting dry mixture was evenly ground, thereby producing  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$ .  $\text{LiOH}$  was added to the  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$  to provide 1 equivalent of lithium, and ethanol was added to facilitate a reaction between the  $\text{LiOH}$  and  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$  and the mixture was mortar/grinder mixed until liquid ethanol disappeared from the mixture.

Thereafter, the mixture was placed in an alumina crucible and heat-treated at  $400^\circ\text{C}$  in a stream of dry air, and then heat-treated again for 12 hours at  $750^\circ\text{C}$ . In both the heat-treating processes, the temperature was raised at a rate of  $3^\circ\text{C}/\text{min}$ . The mixture was allowed to stand at the first and second heat-

treating temperatures for predetermined times, and the mixture was slowly cooled to produce a  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder.

The  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder was then dipped in a Mg-methoxide suspension for about 10 minutes and the coated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder was then separated from the suspension. Subsequently, the powder was dried in an oven at  $120^\circ\text{C}$  for about 5 hours, thereby producing  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder coated with the Mg-methoxide. The powder was then heat-treated at a temperature of  $500^\circ\text{C}$  for about 10 hours in a stream of dry air, thereby producing a positive active material.

Using the positive active material, a coin-type half-cell was fabricated according to the method used in Example 1.

(Example 6)

A coin-type half-cell was fabricated by the same procedure in Example 5 except that  $\text{Ni}(\text{OH})_2$  was mixed with  $\text{Co}(\text{OH})_2$  in an equivalence ratio of 0.9:0.1, thereby producing a positive active material having a formula of  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ .

(Example 7)

A coin-type half-cell was fabricated by the same procedure as in Example 5 except that the Mg-methoxide coated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder was heat-treated at  $600^\circ\text{C}$ .

(Example 8)

A coin-type half-cell was fabricated by the same procedure as in Example 6 except that the Mg-methoxide coated  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  powder was heat-treated at  $600^\circ\text{C}$ .

(Example 9)

LiOH and  $\text{Co}(\text{OH})_2$  were mixed in a 1:1 mole ratio. A sufficient amount of ethanol was added to the mixture to fabricate the reaction, and the mixture was mixed in a mechanical mortar mixer for about 1 hour until liquid solvent disappeared from the mixture.

The mixed powder was placed in an aluminous crucible and heat-treated for 5 hours at  $400^\circ\text{C}$  in a stream of dry air, then heat-treated again for 12 hours at  $750^\circ\text{C}$ . In both the heat-treating processes, the temperature was raised at a rate of  $3^\circ\text{C}/\text{min}$ . The mixture was allowed to stand at the first and the second heat-treating temperatures for predetermined period of time and was slowly cooled to produce a  $\text{LiCoO}_2$  powder.

The  $\text{LiCoO}_2$  powder was then dipped in a Mg-methoxide suspension for about 10 minutes, and the coated  $\text{LiCoO}_2$  powder was then separated from the suspension. Subsequently, the powder was dried in an oven at  $120^\circ\text{C}$  for about 5 hours, thereby producing  $\text{LiCoO}_2$  powder coated with the Mg-methoxide. The powder was then heat-treated at a temperature of  $600^\circ\text{C}$  for about 10 hours in a stream of dry air, thereby producing a positive active material.

Using the positive active material, a coin-type half-cell was fabricated according by the method used in Example 1.

(Example 10)

A coin-type half-cell was fabricated by the same procedure as in Example 9 except that the Mg-methoxide coated  $\text{LiCoO}_2$  powder was heat-treated at a temperature of  $700^\circ\text{C}$ .

(Example 11)

A coin-type half-cell was fabricated by the same procedure as in Example 5 except that the Mg-methoxide coated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder was heat-treated at a temperature of  $700^\circ\text{C}$ .

(Example 12)

$\text{Ni}(\text{OH})_2$ ,  $\text{Co}(\text{OH})_2$ , and  $\text{Al}(\text{OH})_3$  were mixed in an equivalence ratio of 0.8:0.15:0.05 and dispersed in water. The resulting mixture was mixed well by milling with an attritor for about 60 minutes at 450 rpm. The mixed powder was dried in a drying oven at  $120^\circ\text{C}$  for about 24 hours and the resulting dry mixture was evenly ground, thereby producing  $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}(\text{OH})_2$ .  $\text{LiOH}$  was added to the  $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}(\text{OH})_2$  to make 1 equivalent of lithium per formula weight of the hydroxide, and ethanol was added to facilitate the reaction between the  $\text{LiOH}$  and  $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}(\text{OH})_2$ . The mixture was mixed in a mortar until liquid ethanol disappeared from the mixture.

The mixed mixture was placed in an alumina crucible and heat-treated at  $400^\circ\text{C}$  in a stream of dry air, then heat-treated again for 12 hours at  $750^\circ\text{C}$ . In both heat-treating processes, the temperature was raised at a rate of  $3^\circ\text{C}/\text{min}$ . The mixture was allowed to stand at the first and the second heat-treating temperatures for predetermined period of time and was slowly cooled to produce a  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powder.

The  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powder was then dipped in a Mg-methoxide suspension for about 10 minutes and the coated  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powder was then separated from the suspension. Subsequently, the powder was dried

in an oven at 120°C for about 5 hours, thereby producing  $\text{LiNi}_{0.9}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powder coated with the Mg-methoxide. The powder was then heat-treated at a temperature of 700°C for about 10 hours in a stream of dry air, thereby producing a positive active material.

Using the positive active material, a coin-type half-cell was manufactured according to the method used in Example 1.

(Example 13)

$\text{Ni}(\text{OH})_2$ ,  $\text{Co}(\text{OH})_2$ , and  $\text{Sr}(\text{OH})_2$  were mixed in an equivalence ratio of 0.9:0.098:0.002 and dispersed in water. The resulting mixture was mixed well by milling with an attritor for about 60 minutes at 450 rpm. The mixed powder was dried in a drying oven at 120°C for about 24 hours, and the resulting dry mixture was evenly ground, thereby producing  $\text{Ni}_{0.9}\text{Co}_{0.098}\text{Sr}_{0.002}(\text{OH})_2$ . LiOH was added to the  $\text{Ni}_{0.9}\text{Co}_{0.098}\text{Sr}_{0.002}(\text{OH})_2$  to provide 1 equivalent of lithium, and ethanol was added to facilitate a reaction between the LiOH and  $\text{Ni}_{0.9}\text{Co}_{0.098}\text{Sr}_{0.002}(\text{OH})_2$ . The mixture was mixed in a mortar until liquid ethanol disappeared from the mixture.

Thereafter, the mixed mixture was placed in an alumina crucible and heat-treated at 400°C in a stream of dry air, then heat-treated again for 12 hours at 750°C. In both the heat-treating processes, the temperature was raised at a rate of 3°C/min. The mixture was allowed to stand at the first and the second heat-treating temperatures for predetermined period of time, and the mixture was slowly cooled to produce a crystalline  $\text{LiNi}_{0.9}\text{Co}_{0.098}\text{Sr}_{0.002}\text{O}_2$  powder.

The  $\text{LiNi}_{0.9}\text{Co}_{0.098}\text{Sr}_{0.002}\text{O}_2$  powder was then dipped in a Mg-methoxide

suspension for about 10 minutes and the coated  $\text{LiNi}_{0.9}\text{Co}_{0.098}\text{Sr}_{0.002}\text{O}_2$  powder was then separated from the suspension. Subsequently, the powder was dried in an oven at  $120^\circ\text{C}$  for about 5 hours, thereby producing  $\text{LiNi}_{0.9}\text{Co}_{0.098}\text{Sr}_{0.002}\text{O}_2$  powder coated with the Mg-methoxide. The powder was then heat-treated at a temperature of  $700^\circ\text{C}$  for about 10 hours in a stream of dry air, thereby producing of a positive active material.

Using the positive active material, a coin-type half-cell was manufactured according to the method used in Example 1.

(Example 14)

A commercial  $\text{LiCoO}_2$  powder having average particle diameter of  $5\mu\text{m}$  was dipped in a Mg-methoxide suspension for about 10 minutes and the coated  $\text{LiCoO}_2$  powder was then separated from the suspension. This powder was then dried in an oven at  $120^\circ\text{C}$  for about 5 hours, thereby producing  $\text{LiCoO}_2$  powder coated with Mg-methoxide. The Mg-methoxide coated  $\text{LiCoO}_2$  powder was subsequently heat-treated for about 10 hours at  $600^\circ\text{C}$  in a stream of dry air to produce a positive active material.

(Example 15)

A commercial  $\text{LiCoO}_2$  powder having average particle diameter of  $5\mu\text{m}$  was dipped in an Al-isopropoxide suspension for about 10 minutes, and the coated  $\text{LiCoO}_2$  powder was then separated from the suspension. This powder was then dried in an oven at  $120^\circ\text{C}$  for about 5 hours, thereby producing  $\text{LiCoO}_2$  powder coated with Al-isopropoxide. The Al-isopropoxide  $\text{LiCoO}_2$  powder was subsequently heat-treated for about 10 hours at  $600^\circ\text{C}$  in a stream

of dry air to produce a positive active material.

(Example 16)

A commercial  $\text{LiCoO}_2$  powder having average particle diameter of  $10\mu\text{m}$  was dipped in a Mg-methoxide suspension for about 10 minutes and then separated from the suspension. This powder was then dried in an oven at  $120^\circ\text{C}$  for about 5 hours, thereby producing  $\text{LiCoO}_2$  powder coated with Mg-methoxide. The Mg-methoxide  $\text{LiCoO}_2$  powder was subsequently heat-treated for about 10 hours at  $600^\circ\text{C}$  in a stream of dry air to produce a positive active material.

The positive active material, a conductive agent (carbon, product name: Super P), a binder (polyvinylidene fluoride, product name: KF-1300) and a solvent (N-methyl pyrrolidone) were mixed to produce a positive active material slurry. The slurry was then cast into a tape on an Al foil to prepare a positive electrode.

Using the positive electrode; a negative electrode made from MCF (meso-carbon fiber) material; an organic electrolyte including 1M  $\text{LiPF}_6$  in a mixture of ethylene carbonate, dimethyl carbonate and diethyl carbonate in a 3:3:1 volume ratio; and a sheet of microporous polypropylene separator (Ashai Company), a 18650-size cylindrical cell having a capacity of 1650mAh was fabricated. The cycle-life characteristics of this cell were then measured at 1C rate in the voltage range of 2.75 to 4.2V.

(Example 17)

$\text{LiCoO}_2$  powder having average particle diameter of  $5\mu\text{m}$  was dipped in an Al-isopropoxide suspension for about 10 minutes and then separated from

the suspension. This powder was then dried in an oven at 120°C for about 5 hours, thereby producing  $\text{LiCoO}_2$  powder coated with Al-isopropoxide. The Al-isopropoxide coated  $\text{LiCoO}_2$  powder was subsequently heat-treated for about 10 hours at 600°C in a state where dry air was blown on the powder to produce active material for a positive electrode used in lithium-ion cell.

Using this active material, a positive electrode and a cell were fabricated using the same method as in Example 16.

(Example 18)

$\text{Ni(OH)}_2$  and  $\text{Co(OH)}_2$  were mixed in an equivalence ratio of 0.8:0.2 and dispersed in water. The mixture was mixed well by milling with an attritor for about 60 minutes at 450 rpm. The mixed powder was dried in a drying oven at 120°C for about 24 hours and the resulting dried mixture was evenly ground, thereby producing  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$ . LiOH was added to the  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$  to make 1 equivalent of lithium per formula weight of the hydroxide, and ethanol was added to facilitate the reaction between the LiOH and  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$ . The mixture was mixed in a mortar until liquid ethanol disappeared from the mixture.

Thereafter, the mixed mixture was placed in an alumina crucible and heat-treated at 400°C in a stream of dry air, then heat-treated again for 12 hours at 750°C. In both the heat-treating processes, the temperature was raised at a rate of 3°C/min. The mixture was allowed to stand at the first and the second heat-treating temperatures for predetermined period of time, and the mixture was slowly cooled to produce a  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder.



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The  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder was then dipped in a Mg-methoxide suspension for about 10 minutes, and then separated from the suspension. Subsequently, the powder was dried in an oven at  $120^\circ\text{C}$  for about 5 hours, thereby producing  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder coated with the Mg-methoxide. The powder was then heat-treated at a temperature of  $500^\circ\text{C}$  for approximately 10 hours in a stream of dry air, thereby producing a positive active material.

The positive active material, a conductive agent (carbon, product name: Super P), a binder (polyvinylidene fluoride, product name: KF-1300) and a solvent (N-methyl pyrrolidone) were mixed to produce a positive active material slurry. The slurry was then cast into a tape on an Al foil to prepare a positive electrode.

Using this positive electrode, a negative electrode made from MCF (meso-carbon fiber) material, an organic electrolyte including 1M  $\text{LiPF}_6$  in a mixture of ethylene carbonate, dimethyl carbonate and diethyl carbonate in a 3:3:1 volume ratio, and a sheet of microporous polypropylene separator (Ashai Company), a 18650-size cylindrical cell having a capacity of 1650mAh was fabricated. The cycle-life characteristics of this cell were then measured at 1C rate in the voltage range of 2.75 to 4.2V.

(Example 19)

20 A coin-type half-cell was fabricated by the same procedure as in Example 8 except that  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  was coated with an Al-isopropoxide suspension.

(Example 20)

A coin-type half-cell was fabricated by the same procedure as in

Example 9 except that an Al-isopropoxide suspension was used instead of the Mg-methoxide suspension.

(Example 21)

A coin-type half-cell was fabricated by the same procedure as in Example 10 except that an Al-isopropoxide suspension was used instead of the Mg-methoxide suspension.

(Example 22)

A coin-type half-cell was fabricated by the same procedure as in Example 14 except that an Al-isopropoxide suspension was used instead of the Mg-methoxide suspension.

(Example 23)

A coin-type half-cell was fabricated by the same procedure as in Example 16 except that an Al-isopropoxide suspension was used instead of the Mg-methoxide suspension.

(Comparative Example 1)

A coin-type half-cell was fabricated by the same procedure as in Example 1 except that the step of coating the semi-crystalline  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder with the Mg-methoxide suspension was omitted.

(Comparative Example 2)

A coin-type half-cell was fabricated by the same procedure as in Example 2 except that the step of coating the semi-crystalline  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder with the Mg-methoxide suspension was omitted.

(Comparative Example 3)

A coin-type half-cell was fabricated by the same procedure as in

Example 5 except that the step of coating the semi-crystalline  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder with the Mg-methoxide suspension was omitted.

(Comparative Example 4)

$\text{Ni}(\text{OH})_2$ ,  $\text{Co}(\text{OH})_2$ , and  $\text{Mg}(\text{OH})_2$  were mixed in an equivalence ratio of 0.8:0.15:0.05 and dispersed in water. The resulting mixture was mixed well by milling with an attritor for about 60 minutes at 450 rpm. The mixed powder was dried in a drying oven at  $120^\circ\text{C}$  for about 24 hours and the resulting dry mixture was evenly ground, thereby producing  $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Mg}_{0.05}(\text{OH})_2$ . LiOH was added to the  $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Mg}_{0.05}(\text{OH})_2$  to make 1 equivalent of lithium per formula weight of the hydroxide, and ethanol was added to facilitate a reaction between the LiOH and  $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Mg}_{0.05}(\text{OH})_2$ . The mixture was mixed in a mortar until liquid ethanol disappeared from the mixture. The mixed mixture was placed in an alumina crucible and heat-treated at  $400^\circ\text{C}$  in a stream of dry air, then heat-treated again for 12 hours at  $750^\circ\text{C}$  to produce a positive active material.

Using the positive active material, a coin-type half-cell was fabricated according to the method used in Example 1.

(Comparative Example 5)

A coin-type half-cell was fabricated by the same procedure as in Example 9 except that the step of coating the semi-crystalline  $\text{LiCoO}_2$  powder with the Mg-methoxide suspension was omitted.

(Comparative Example 6)

A coin-type half-cell was fabricated by the same procedure as in Example 11 except that the step of coating the semi-crystalline  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$

powder with the Mg-methoxide suspension was omitted.

(Comparative Example 7)

A coin-type half-cell was fabricated by the same procedure as in Example 12 except that the step of coating the semi-crystalline  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powder with the Mg-methoxide suspension was omitted.

(Comparative Example 8)

A coin-type half-cell was fabricated by the same procedure as in Example 13 except that the step of coating the semi-crystalline  $\text{LiNi}_{0.9}\text{Co}_{0.098}\text{Sr}_{0.002}\text{O}_2$  powder with the Mg-methoxide suspension was omitted.

(Comparative Example 9)

$\text{LiCoO}_2$  powder having average particle diameter of  $5\mu\text{m}$  was used as a positive active material for a coin-type half-cell.

(Comparative Example 10)

A coin-type half-cell was fabricated by the same procedure as in Example 16 except that the step of coating the semi-crystalline  $\text{LiCoO}_2$  powder with the Mg-methoxide suspension was omitted.

(Comparative Example 11)

A cell as disclosed in the Matsushita Technical Journal Vol. 44, August 1998, pp. 407-412 was used for Comparative Example 11.

(Comparative Example 12)

A 18650-size cylindrical cell was fabricated by the same procedure as in Example 18 except that the step of coating the semi-crystalline  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder with the Mg-methoxide suspension was omitted.

(Comparative Example 13)

A coin-type half-cell was fabricated by the same procedure as in Example 19 except the step of coating the semi-crystalline  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  powder with the Al-isopropoxide suspension was omitted.

(Comparative Example 14)

$\text{LiCoO}_2$  was mixed a commercial  $\text{Al}_2\text{O}_3$ . Using the resulting mixture, a coin-type half-cell was fabricated by the same procedure as in Comparative example 1.

(Comparative Example 15)

$\text{LiCoO}_2$  powder was intimately mixed by grinding with about 1% by weight of  $\text{Al}_2\text{O}_3$  and the mixture was then briefly heated at about  $800^\circ\text{C}$  for 1 hour to positive active material. Using the resulting positive active material, a coin-type coin-cell was fabricated by the same procedure as in Comparative example 1.

FIGs. 1A and 1B show SEM pictures, respectively 200-times and 20,000-times expanded view of the positive active material according to Example 1; and FIGs. 2A and 2B show SEM pictures, respectively 300-times and 20,000-times expanded view of the positive active material according to Comparative Example 1. As shown in FIGs. 1A and 2A, the positive active material according to Example 1 is comprised of clumps that are less than  $100\text{ }\mu\text{m}$  in size, whereas the positive active material according to Comparative Example 1 is comprised of clumps that are greater than  $100\text{ }\mu\text{m}$  in size. Further, as shown in FIG. 1B, the positive active material according to Example 1 is comprised of ultra-fine particles of  $0.1$  to  $0.2\text{ }\mu\text{m}$  in size which aggregate mass

together to form small particles of 0.5 to 1 $\mu$ m in size. On the other hand, as shown in FIG. 2B, the positive active material according to Comparative Example 1 is comprised of particles that are greater than 1 $\mu$ m in size which aggregate together into clumps.

FIG. 3 shows a graph of XRD patterns of the positive active material according to Example 2 and Comparative Example 2. As shown in the drawing, an XRD pattern (a in FIG. 3) of the semi-crystalline  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder produced by mixing  $\text{LiOH}$  and  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$  in the acetone solvent followed by heat-treating at a temperature of 500 $^{\circ}\text{C}$  for the first heat-treatment step only is broad and has peaks that are not significantly high, indicative of a semi-crystalline state. Further, an XRD pattern (b in FIG. 3) of the  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder produced by mixing  $\text{LiOH}$  and  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$  in the acetone solvent then heat-treating at a temperature of 500 $^{\circ}\text{C}$  for the first heat-treatment step and heat-treating at a temperature of 750 $^{\circ}\text{C}$  for the second heat-treatment step has sharp peaks, which indicates a complete crystalline state. This XRD pattern is substantially identical to an XRD pattern (c in FIG. 3) of the crystalline positive active material of Comparative Example 2 in which Mg is not coated. Since the XRD pattern of the positive active material of Example 2 (b in FIG. 3) is identical to that of the active material in which Mg is not coated (c in FIG. 3), the results indicate that the Mg-oxide does not penetrate into the crystalline structure of the positive active material, but coats the surface of the crystalline structure. In FIG. 3, “\*” indicates Si reference peaks.

FIG. 4 shows a graph of cycle-life characteristics of coin-type cells

prepared according to Example 1 (a in FIG. 4), Example 3 (b in FIG. 4) and Comparative Example 1 (c in FIG. 4). A capacity and a cycle life of each of the cells were measured by charging-discharging the cells in the voltage range of 2.8V to 4.3V, at 0.1C (1 cycle), 0.2C (3 cycles), 0.5C (10 cycles), and 1C (85 cycles) rates. As shown in FIG. 4, when charge and discharge at a high rate of 1C, the capacity of the cell according to Example 1 reduced from 72.8 mAh/g to 66.8 mAh/g (approximately 8%) after 85 cycles, and the capacity of the cell according to Example 3 reduced from 122 mAh/g to 77.5mAh/g (approximately 36%) after 85 cycles. On the other hand, the capacity of the cell according to Comparative Example 1 reduced from 111.9 mAh/g to 42.6 mAh/g (approximately 60%) after 85 cycles. In summary, the results indicate that the positive active materials of Examples 1 and 3 are more stable in high-rate cycling, therefore improved cycle-life over that of Comparative Example 1.

FIGs. 5A and 5B show SEM pictures of the positive active material according to Example 5 and Comparative Example 3, respectively. As shown in FIGs. 5A and 5B, the surface of the active material of Example 5 is apparently different from the surface of the active material of Comparative Example 3 as a result of the metal oxide coating on the surface of the active material.

XRD patterns of the positive active materials of Example 5, Comparative Example 3 and Comparative Example 4 are shown respectively by lines (A), (B) and (C) of FIG. 6. In FIG. 6, “\*” indicates Si reference peaks. In FIG. 6, with regard to lattice parameters, a-axis is 2.876 and c-axis is 14.151 in the case of (a), a-axis is 2.883 and c-axis is 14.150 in the case of (b), and a-axis is 2.872

and c-axis is 14.204 in the case of (c). As shown in FIG. 6, significantly different XRD patterns are shown for the positive active material of Example 5 (A) compared to the XRD patterns of the positive active material of Comparative Example 4 (C) in which Mg is doped within the structure of the active material instead of being coated, whereas the XRD pattern of the active material of Example 5 is substantially identical to that of the active material of Comparative Example 3 (B) in which Mg is neither doped nor coated on the active material. The results indicate that the active material of Example 5 maintains the structure of the original active material which is not coated with Mg indicating that the Mg stay at the surface without penetrating into the bulk of the material. The results also indicate that the electro-chemical characteristics, are improved by the surface coating.

FIG. 7 shows a graph of cycle-life characteristics of the cells according to Example 5 and Comparative Example 3 in the voltage range of 2.8V to 4.3V. In FIG. 7, the curve (a) corresponds to Example 5 and the curve (b) corresponds to Comparative Example 3. As shown in FIG. 7, the capacity of the cell for 1C-rate cycling of Example 5 reduced from 140 mAh/g to 90 mAh/g, while that of Comparative Example 3 reduced from 140 mAh/g to 60 mAh/g, showing that the cell capacity of Example 5 has reduced significantly more than that of Comparative Example 3 in the 1C-rate cycling.

FIG. 8 shows DSC analysis results of the cells according to Example 9 (b in FIG. 8) and Comparative Example 5 (a in FIG. 8). These results were obtained using electrodes from the cells charged at 4.1V. The DSC analysis result illustrates the thermal stability of individual sample cells. After charging



the cell, the positive active material is converted from  $\text{LiCoO}_2$  to  $\text{Li}_{1-x}\text{CoO}_2$  ( $0.5 \leq x < 1$ ). The charged active material,  $\text{Li}_{1-x}\text{CoO}_2$ , becomes unstable as temperature is increased releasing oxygen gas due to weakened Co-O bonds, showing an exothermic peak in the DSC curve. The released oxygen may react with the electrolyte in the cell causing the cell to explode in the worst case. Both the peak temperature and the peak size which represent the amount of heat released are a measure of the instability of the charge material of the cell.

As shown in FIG. 8, the exothermic peak temperature for Comparative Example 5 is about  $213^\circ\text{C}$ , while that for Example 9 is about  $5^\circ\text{C}$  higher (approximately  $218^\circ\text{C}$ ) than that for Comparative Example 5. The amount of heat released (peak size) for Example 9 is about half that of Comparative Example 5. It is apparent that the Mg coating on the  $\text{LiCoO}_2$  powder improve the stability of the charged active material,  $\text{Li}_{1-x}\text{CoO}_2$ . This improved stability might be due to the fact that the cobalt-magnesium coating layer may limit the access of the charged positive active material to the electrolyte, thereby reducing the oxidation of the electrolyte.

FIG. 9 shows a graph illustrating cycle-life characteristics during charging and discharging the cells of Example 9 and Comparative Example 5 in the voltage range of 2.75V to 4.1V. In FIG. 9, (a) corresponds to the cell of Example 9, while (b) corresponds to the cell of Comparative Example 5. In the case of Comparative Example 5, during 100 charge-discharge cycles at 1C rate, the capacity of the cell is reduced from 108 mAh/g to 38 mAh/g (a reduction of 65%), whereas the capacity of the cell of Example 9 is reduced from 114mAh/g

to 70mAh/g (a reduction of 39%) under similar cycling conditions. Relative to Comparative Example 5, the capacity fading of Example 9 is considerably smaller at a high rate (1C rate), therefore showing improved cycle life.

FIG. 10 shows a graph illustrating cycle-life characteristics during charging and discharging in the voltage range of 2.75V to 4.2V of the cell according to Example 9 and Comparative Example 5. In FIG. 10, the curve (a) corresponds to the cell of Example 9 and the curve (b) corresponds to the cell of Comparative Example 5. In the case of Comparative Example 5, after 100 charge-discharge cycles at 1C rate, the capacity of the cell reduced from 120 mAh/g to 15 mAh/g (a reduction of 88%), whereas the capacity of the cell of Example 9 is reduced from 129 mAh/g to a low of 96 mAh/g (a reduction of only 26%). Accordingly, relative to Comparative Example 5, the capacity fading is considerably smaller at a high rate and cycle life is significantly greater for Example 9.

FIG. 11 shows a graph of cycle-life characteristics during charging and discharging in the voltage range of 2.75V to 4.3V of the cells according to Example 9 and Comparative Example 5. In FIG. 11, the curve (a) corresponds to the cell of Example 9 and the curve (b) corresponds to the cell of Comparative Example 5. Accordingly, relative to Comparative Example 5, the capacity fading is considerably smaller at a high rate and cycle life is significantly greater for Example 9.

FIG. 12 illustrates XRD analysis results of the positive active materials according to Example 10 and Comparative Example 5. The curve (a) indicates XRD analysis results of the  $\text{LiCoO}_2$  positive active material according to

Comparative Example 5. The curve (b) indicates XRD analysis results of the positive active material according to Example 10 after the cell was charged at 4.2V, and the curve (c) indicates XRD analysis results of the positive active material according to Comparative Example 5 after the cell was charged at 4.2V. As shown in (a) and (c) of FIG. 12, it indicates that as a result of charging, the structure of  $\text{LiCoO}_2$  changes from a hexagonal structure to a monoclinic structure (reference, J. Electro. Chem. Soc. Vol. 143, No. 3, 1006, p. 1114-1122). On the other hand, the  $\text{LiCoO}_2$  powder of Example 10 maintains its hexagonal structure even after charging, indicative of a stable surface obtained as a result of the coating of the magnesium oxide.

Referring to FIG. 13, the curve (b) illustrates DSC analysis results of the cell of Example 10 after the cell was charged at 4.2V, and the curve (a) illustrates DSC analysis results of the cell of Comparative Example 5 after the cell was charged at 4.2V. As shown in FIG. 13, an exothermic peak temperature for the oxygen release is  $211^\circ\text{C}$  for Comparative Example 5, while it is  $227^\circ\text{C}$  for Example 10. Accordingly, Example 10 has about a  $16^\circ\text{C}$  higher oxygen release temperature than Comparative Example 5.

In FIG. 14, the curve (b) illustrates DSC analysis results of the cell of Example 10 after the cell was charged at 4.1V, and the curve (a) illustrates DSC analysis results of the cell of Comparative Example 5 after the cell was charged at 4.1V. As shown in FIG. 14, an exothermic peak temperature for the oxygen release is  $213^\circ\text{C}$  for Comparative Example 5, while it is  $227^\circ\text{C}$  for Example 10. Accordingly, Example 10 has about a  $15^\circ\text{C}$  higher oxygen decomposition

temperature than Comparative Example 5, and the amount exothermic heat for Example 10 is about half that of Comparative Example 5.

Referring to FIG. 15, (b) illustrates DSC analysis results of the cell of Example 11 after the cell was charged at 4.1V, and (a) illustrates DSC analysis results of the cell of Comparative Example 6 after the cell was charged at 4.1V. As shown in FIG. 15, the cell according to Comparative Example 6 emits heat of about 20mW at 223°C, while the cell according to Example 11 emits heat of about 6mW at 232°C. Accordingly, Example 11 has about a 9°C higher oxygen decomposition peak temperature than Comparative Example 6, and the amount of exothermic heat for Example 11 is about one-third that of Comparative Example 6.

Referring to FIG. 16, (b) illustrates DSC analysis results of the cell of Example 12 after the cell was charged at 4.3V, and (a) illustrates DSC analysis results of the cell of Comparative Example 7 after the cell was charged at 4.3V. As shown in FIG. 16, the cell of Comparative Example 7 emits exothermic heat of about 15mW at 213°C, and the cell of Example 12 emits heat of about 10mW at 225°C. Accordingly, Example 12 has about a 12°C higher oxygen decomposition peak temperature than Comparative Example 7.

Referring to FIG. 17, (b) illustrates DSC analysis results of the cell of Example 13 after the cell was charged at 4.3V, and (a) illustrates DSC analysis results of the cell of Comparative Example 8 after the cell was charged at 4.3V. As shown in FIG. 17, the cell according to Comparative Example 8 emits exothermic heat of about 10mW at 217°C, and the cell according to Example 13

emits heat of about 2mW at 227°C. Accordingly, Example 13 has about a 10°C higher oxygen decomposition peak temperature than Comparative Example 8, and the amount of exothermic heat of Example 13 is about one-third that of Comparative Example 8.

FIG. 18 shows a TEM (transmission electron microscope) picture of active material according to Example 14. The  $\text{LiCoO}_2$  active material not coated with Mg-methoxide suspension is a crystalline material having approximately a 5 $\mu\text{m}$  diameter such that the surface of the material is smooth. However, in the active material of Example 14, which is coated with Mg-methoxide suspension then heat-treated, minute particles of approximately 5-15nm surround a periphery of  $\text{LiCoO}_2$ , the particles of a composite of cobalt and magnesium, a metal oxide such as magnesium oxide, etc.

FIG. 19 shows a TEM picture of the active material of Example 15. In Example 15, the active material is coated with Al-isopropoxide and is heat-treated. As shown in FIG. 19, a double layer structure made of a composite metal oxide of cobalt and aluminum or a metal oxide such as aluminum oxide is formed on the surface of the particles of  $\text{LiCoO}_2$ . Accordingly, the active material of the present invention coated with metal alkoxide suspension on its surface then heat-treated clearly has a different form compared to the material that is not processed in this manner.

FIG. 20 shows a graph of cycle-life characteristics of the cells according to Example 16 and Comparative Example 10. The cells of Example 16 and Comparative Example 10 had formation cycles at 0.2C rate, and then were charged-discharged at 1C rate. In FIG. 20, (a) corresponds to Example 16 and

(b) corresponds to Comparative Example 10. In comparing cycle-life characteristics of the cells over 250 cycles, the capacity of Comparative Example 10 reduced by about 30% compared to its initial capacity, while the capacity of Example 16 reduced by only about 20% compared to its initial capacity. It indicates that the cycle life of Example 16 is superior to that of Comparative Example 10.

FIG. 21 shows a graph of discharge curves of the cell according to Example 17. After charging the cell at 0.5C rate, the discharge rate was varied from 0.2C to 0.5C, 1C, and 2C to measure cell performance at various rates. The cell showed almost full capacity even at 2C rate indicating that it has an excellent rate capability.

FIG. 22 shows a graph of discharge curves of the cell according to Comparative Example 11. In comparing the discharge characteristics of Example 17 of FIG. 21 and Comparative Example 11 of FIG. 22, the characteristics are similar up to 1C rate, but at 2C rate, the amount of reduction in capacity for Example 17 is significantly smaller than Comparative Example 11.

FIG. 23 shows a graph of cycle-life characteristics of the cells according to Example 18 (open circles in the drawing) and Comparative Example 12 (filled circles in the drawing). As shown in FIG. 23, cycle-life characteristics for Example 18 are better than those of Comparative Example 12 up to about 100 cycles, after which the characteristics are substantially similar.

The charge and discharge characteristics of the positive active materials according to Example 19 and Comparative example 13 are presented respectively by lines (B) and (A) of FIG. 24. It was evident from FIG. 24, the

Al<sub>2</sub>O<sub>3</sub> coatings cause to deteriorate capacity and voltage in the Ni-based active material. The result is believed that Al reacts with the Ni-based active material at the surface of the particle and its structure is modified, thereby deteriorating capacity and voltage. These results indicate that a Ni-based positive active material obtained from Japanese Patent Laid-Open Hei. 9-55210 exhibits low capacity and voltage than a Co-based positive active material of the present invention.

To compare the structure of the synthesized Al<sub>2</sub>O<sub>3</sub> of the present invention and the commercial Al<sub>2</sub>O<sub>3</sub> of Comparative example 15, the XRD was measured. The active Al<sub>2</sub>O<sub>3</sub> was prepared by suspending Al-isopropoxide powder in ethanol for 10 hours, drying the resulting suspension at 100 °C for 24 hours to obtain a white powder and heat-treating the white powder at 600 °C for 10 hours. The resulting Al<sub>2</sub>O<sub>3</sub> has amorphous and active properties which are different from the commercial Al<sub>2</sub>O<sub>3</sub> having crystalline and inactive properties. Such a difference is evidently shown in FIG. 25. The line (A) which indicates the XRD result of the inactive Al<sub>2</sub>O<sub>3</sub> in FIG. 25 teaches that it is crystalline and the line (B) which indicates the XRD result of the active Al<sub>2</sub>O<sub>3</sub> in FIG. 25 teaches that it is amorphous.

Each of the active Al<sub>2</sub>O<sub>3</sub> and inactive Al<sub>2</sub>O<sub>3</sub> was added, respectively, to the mixture of the LiCoO<sub>2</sub> positive active material, a polyvinylidene fluoride binder, and a carbon conductive agent to prepare positive active material slurries. Using the prepared positive active material slurries, coin-type half-cells were fabricated. The charge and discharge characteristics of the coin-type half-cells were measured and the results are shown in FIG. 26. For

reference, the charge and discharge characteristic of the coin-type half-cells containing only  $\text{LiCoO}_2$  (A) was shown in FIG. 26. As shown in FIG. 26, the coin-type half-cell containing the active  $\text{Al}_2\text{O}_3$  and  $\text{LiCoO}_2$  (B) (gives higher capacity (about 159 mAh/g) than that containing the inactive  $\text{Al}_2\text{O}_3$  (C) and  $\text{LiCoO}_2$ . These results indicate that the commercial inactive  $\text{Al}_2\text{O}_3$  does not improve the cell performance. It is assumed that the positive active material with the commercial  $\text{Al}_2\text{O}_3$  according to Comparative example 15 (prepared by the procedure in U.S. Patent No. 5,705,291) does not improve cell performance.

The SEM pictures of the positive active materials according to Example 21 and Comparative example 15 are shown in FIGs. 27 and 28, respectively. As shown in FIG. 28, Al is partially doped into  $\text{LiCoO}_2$  in Comparative example 15. In contrast, Al is coated on the  $\text{LiCoO}_2$  in Example 15. This difference is believed that the Al-isopropoxide solution is used in Example 15 and  $\text{Al}_2\text{O}_3$  powder is used in Comparative example 15.

In order to identify the structure of the positive active materials precisely according to Example 21 and Comparative example 15, an EDX analysis was carried out. The results are presented in FIGs. 29 and 30, respectively. It is shown from FIGs. 29 and 30 that the structure of the positive active material according to Example 21 is different from that according to Comparative example 15.

Although the present invention has been described in detail hereinabove, it should be clearly understood that many variations and/or modifications of the basic inventive concepts taught herein, which may appear to those skilled in the



present art, will still fall within the spirit and scope of the present invention, as defined in the appended claims.

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**WHAT IS CLAIMED IS:**

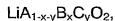
1. A positive active material for a rechargeable lithium battery comprising:

a core comprising at least one compound represented by Formula 1;

and

an active metal oxide shell formed on the core, the metal oxide being capable of stabilizing a structure of the active material:

Formula 1



where  $0 \leq x \leq 0.3$ ,  $0 \leq y \leq 0.01$ ;

A is an element selected from the group consisting of Co and Mn;

B is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al; and

C is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al.

2. The positive active material of claim 1 wherein a metal in the active metal oxide shell is an element selected from the group consisting of Mg, Al, Co, K, Na and Ca.

3. The positive active material of claim 2 wherein the metal in the active metal oxide shell is Al.

4. The positive active material of claim 1 wherein the active metal oxide has an amorphous phase.

5. The positive active material of claim 1 wherein the positive active material is formed of minute particles in an agglomerated state such that a

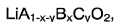
particle size of the active material is between 0.1 and 100 $\mu$ m.

6. The positive active material of claim 1 wherein the positive active material is LiCoO<sub>2</sub>.

7. The positive active material of claim 1 wherein the active metal oxide shell is processed with minute particles of 5-15nm in size.

8. A rechargeable lithium battery comprising a positive active material, the positive active material comprising a core comprising at least one compound represented by Formula 1 and an active metal oxide shell formed on the core, the active metal oxide being capable of stabilizing a structure of the active materials.

Formula 1



where  $0 \leq x \leq 0.3$ ,  $0 \leq y \leq 0.01$ ;

A is an element selected from the group consisting of Co and Mn;

B is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al; and

C is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al.

9. The rechargeable lithium battery of claim 8 wherein the metal in the active metal oxide shell is an element selected from the group consisting of Mg, Al, Co, K, Na and Ca.

10. The rechargeable lithium battery of claim 9 wherein a metal in the active metal oxide shell is Al.

11. The rechargeable lithium battery of claim 8 wherein the active

metal oxide has an amorphous phase.

12. A positive active material for a rechargeable lithium battery comprising:

a core comprising  $\text{LiCoO}_2$ ; and

an active metal oxide shell formed on the core.

13. The positive active material of claim 12 wherein a metal in the active metal oxide shell is an element selected from the group consisting of Mg, Al, Co, K, Na and Ca.

14. The positive active material of claim 13 wherein the metal in the active metal oxide shell is Al.

15. The positive active material of claim 12 wherein the active metal oxide has an amorphous phase.

16. The positive active material of claim 12 wherein the positive active material is formed of minute particles in an agglomerated state such that a particle size of the active material is between 0.1 and  $100\mu\text{m}$ .

17. The positive active material of claim 12 wherein the active metal oxide shell is processed with minute particles of 5-15nm in size.

18. A positive active material for a rechargeable lithium battery prepared by producing a crystalline powder or a semi-crystalline powder of Formula 1;

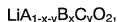
coating the crystalline powder or the semi-crystalline powder with a metal alkoxide suspension; and

heat-treating the coated powder,

the positive active material comprising a core and an active metal oxide

shell formed on the core, the metal oxide being capable of stabilizing the structure of the active material:

Formula 1



where  $0 \leq x \leq 0.3$ ,  $0 \leq y \leq 0.01$ ;

A is an element selected from the group consisting of Co and Mn;

B is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al; and

C is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al.

19. The positive active material of claim 18 wherein a metal in the active metal oxide shell is an element selected from the group consisting of Mg, Al, Co, K, Na and Ca.

20. The positive active material of claim 19 wherein the metal in the active metal oxide shell is Al.

21. The positive active material of claim 18 wherein the active metal oxide has an amorphous phase.

22. The positive active material of claim 18 wherein the positive active material is formed of minute particles in an agglomerated state such that a particle size of the active material is between 0.1 and 100  $\mu\text{m}$ .

23. The positive active material of claim 18 wherein the active metal oxide shell is processed with minute particles of 5-15nm in size.

24. A positive active material for a rechargeable lithium battery comprising:

a core comprising  $\text{LiCoO}_2$ ; and

an active  $\text{Al}_2\text{O}_3$  shell formed on the core.

25. The positive active material for a rechargeable lithium battery of claim 24 wherein the active  $\text{Al}_2\text{O}_3$  has an amorphous phase.

26. The positive active material for a rechargeable lithium battery of claim 24 wherein the positive active material is formed of minute particles in an agglomerated state such that a particle size of the active material is between 0.1 and  $100\mu\text{m}$ .

27. The positive active material of claim 24 wherein the active  $\text{Al}_2\text{O}_3$  shell is processed with minute particles of 5-15nm in size.

### ABSTRACT OF THE DISCLOSURE

Disclosed is a positive active material for a rechargeable lithium battery. The positive active material includes a core including at least one compound represented by Formula 1 and an active metal oxide shell formed on the core.

Formula 1



where  $0 \leq x \leq 0.3$ ,  $0 \leq y \leq 0.01$ , and

A is an element selected from the group consisting of Co and Mn;

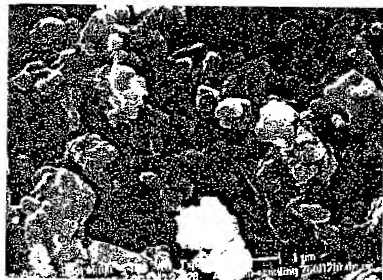
B is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al; and

C is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al.

FIG. 1A



FIG. 1B



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FIG. 2A



FIG. 2B



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FIG. 3

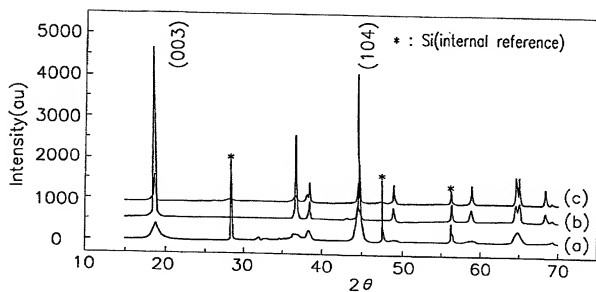


FIG. 4

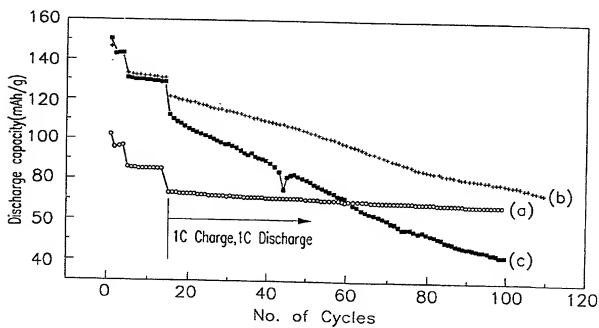


FIG. 5A

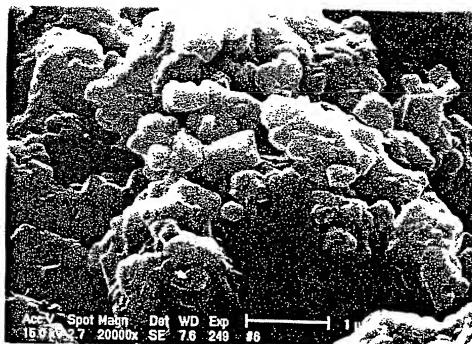
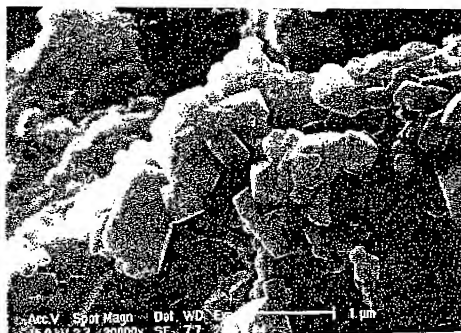


FIG. 5B



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FIG. 6

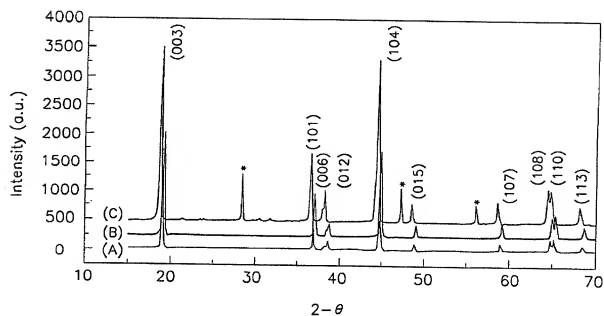


FIG. 7

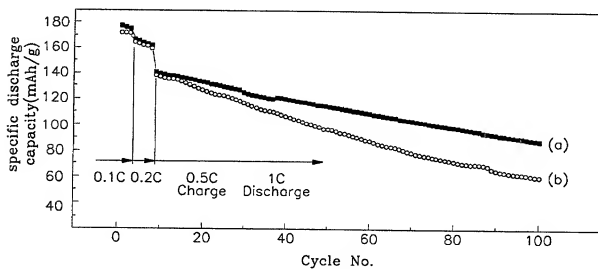


FIG. 8

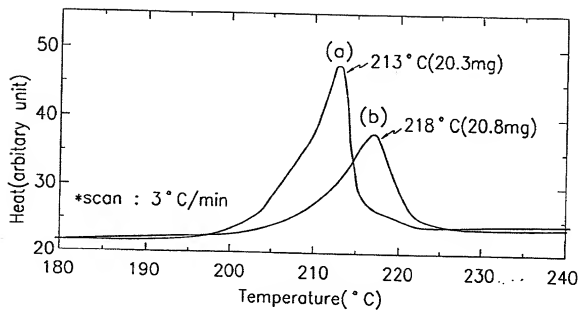


FIG. 9

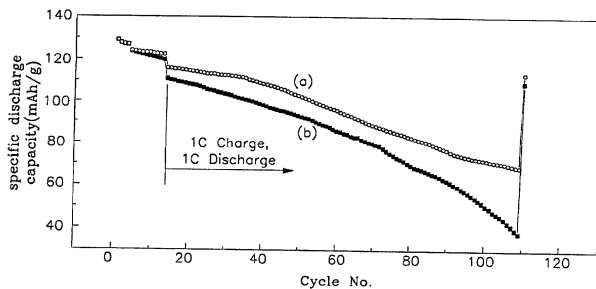
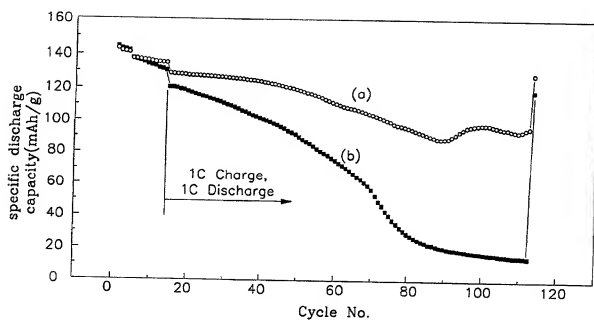


FIG. 10



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FIG. 11

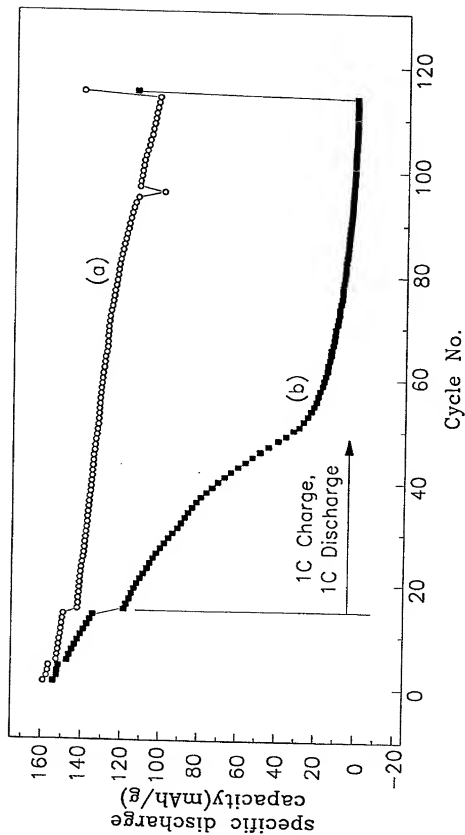


FIG. 12

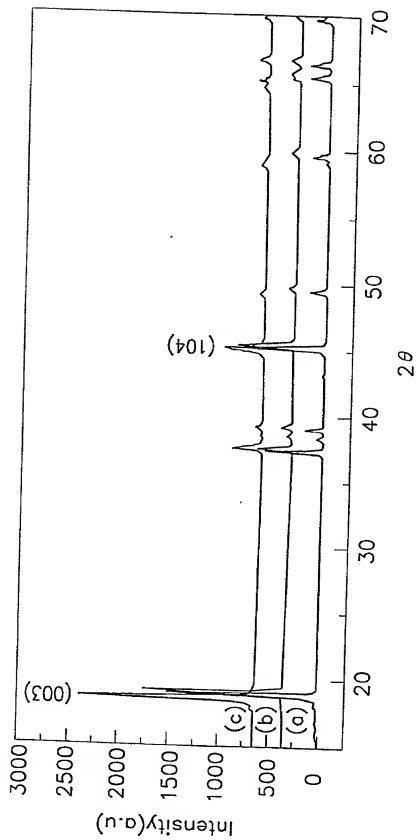




FIG. 13

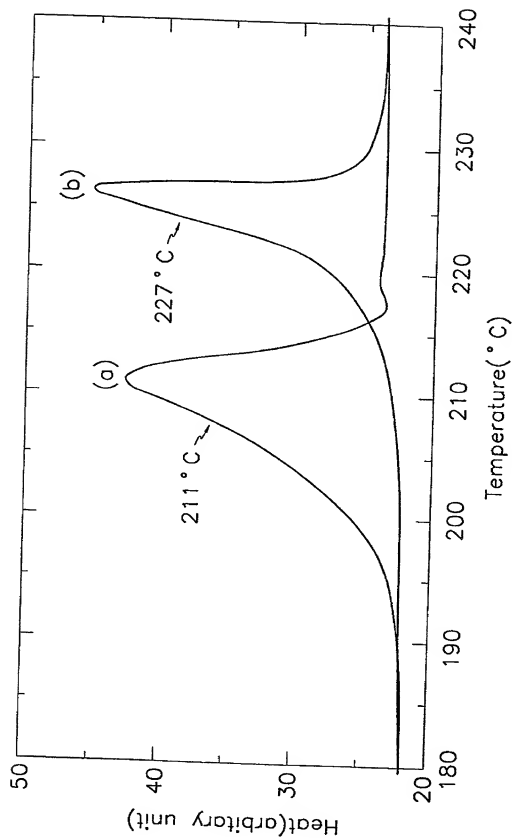


FIG. 14

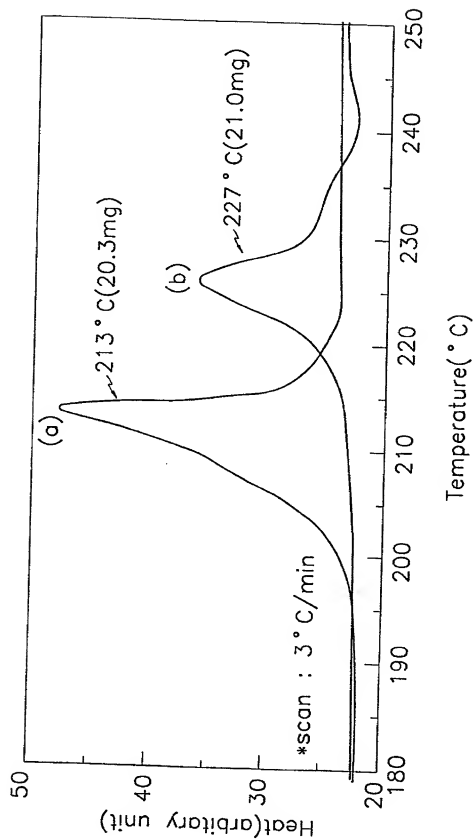


FIG. 15

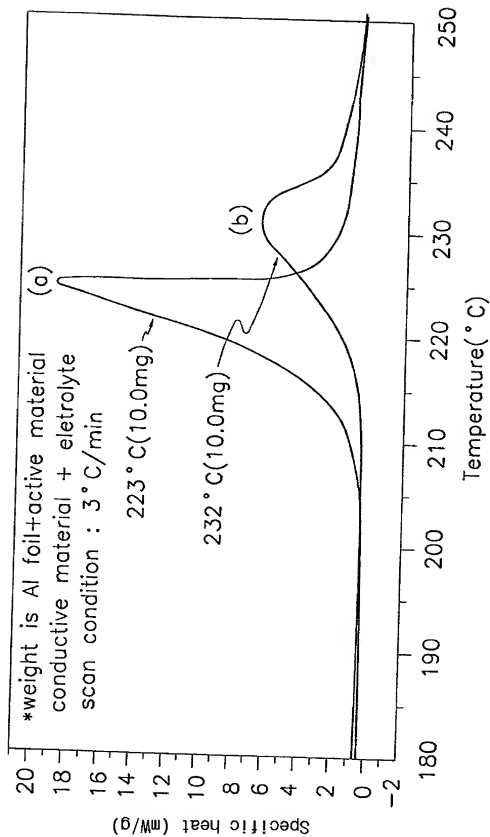


FIG. 16

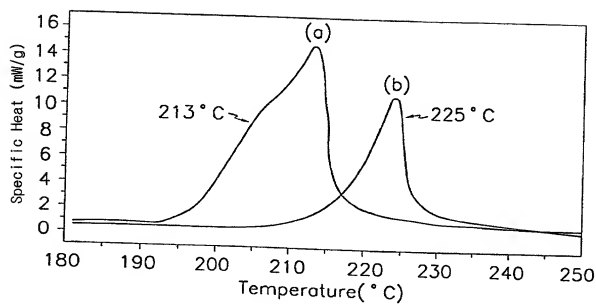


FIG. 17

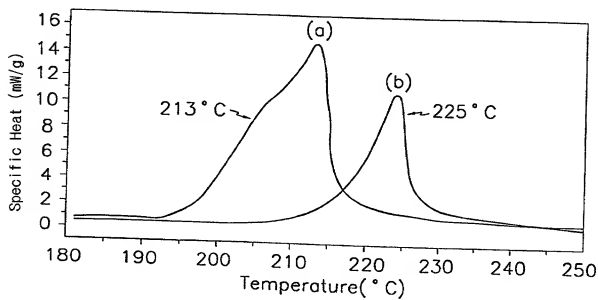


FIG. 18

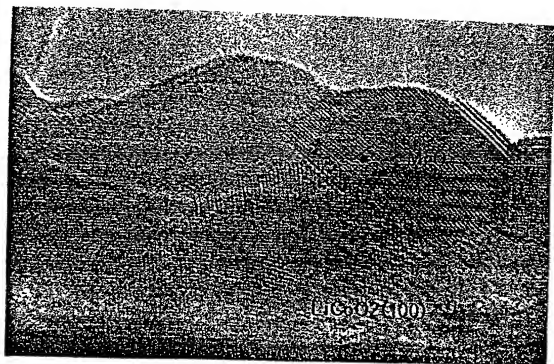


FIG. 19

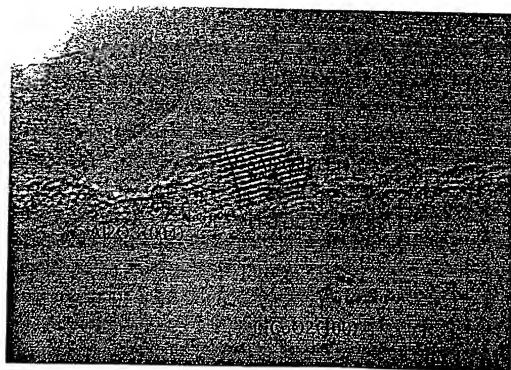


FIG. 20

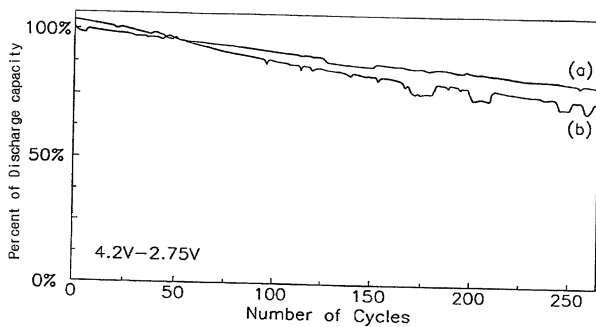


FIG. 21

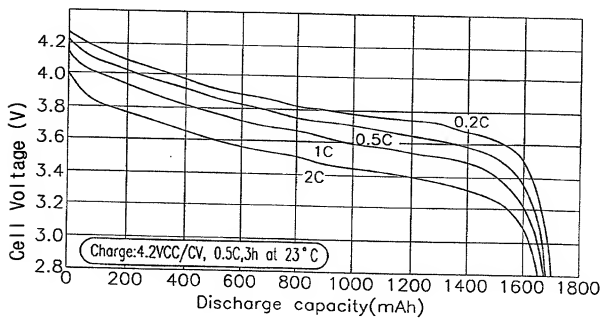


FIG. 22

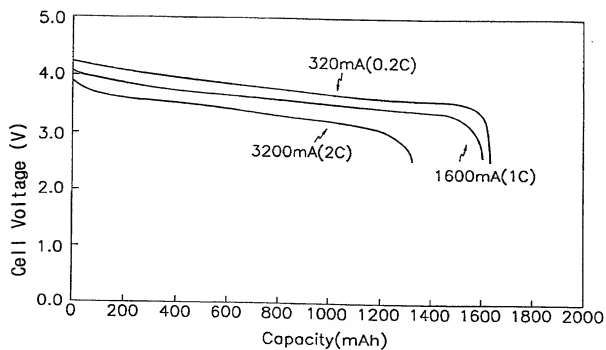


FIG. 23

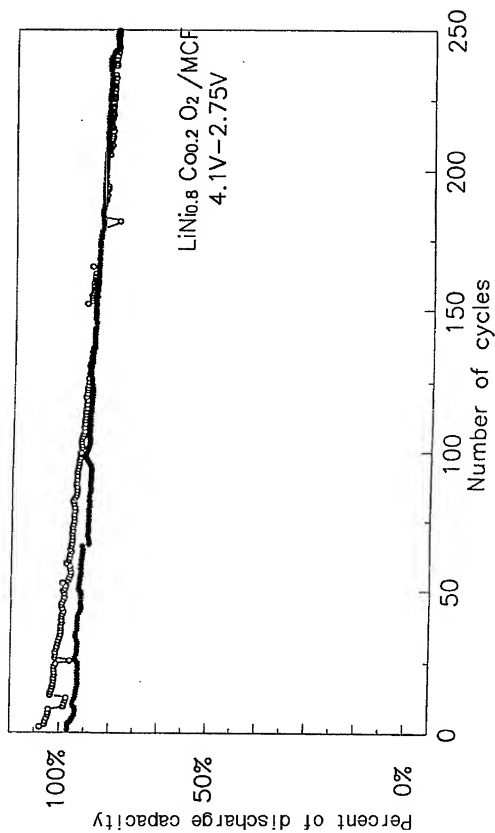




FIG. 24

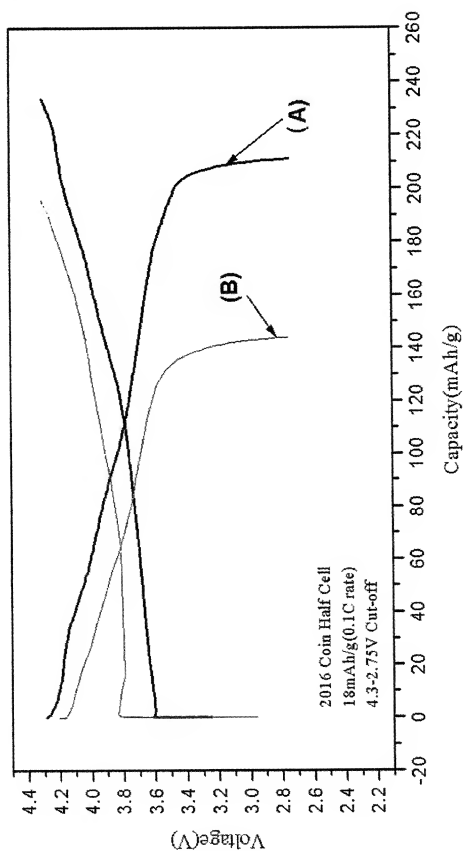


FIG. 25

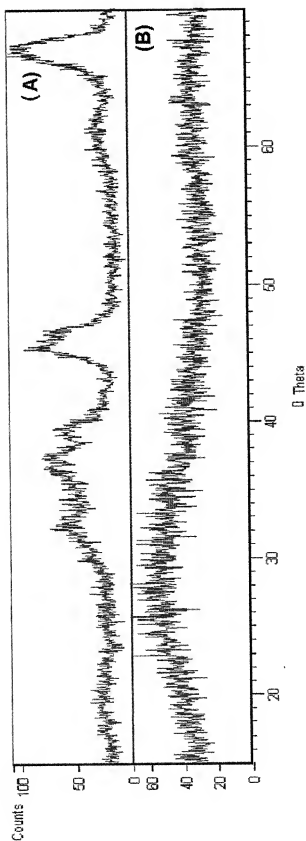


FIG. 26

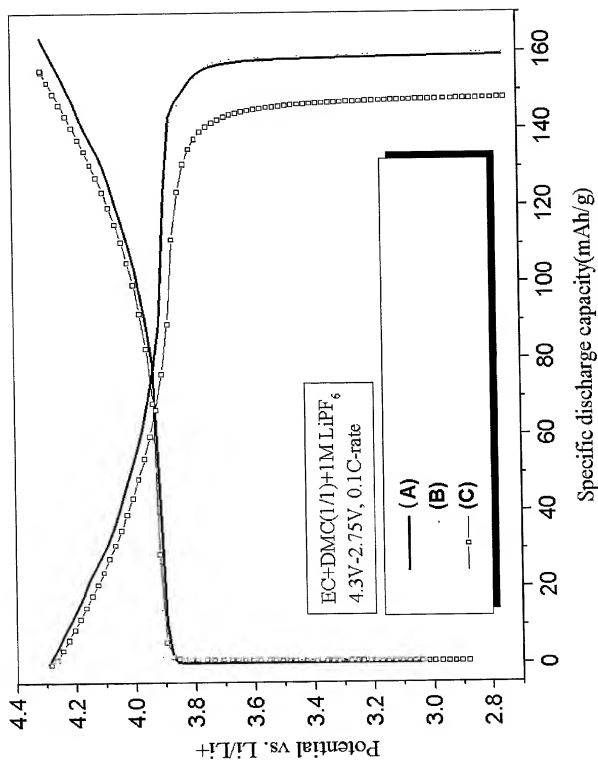


FIG. 27

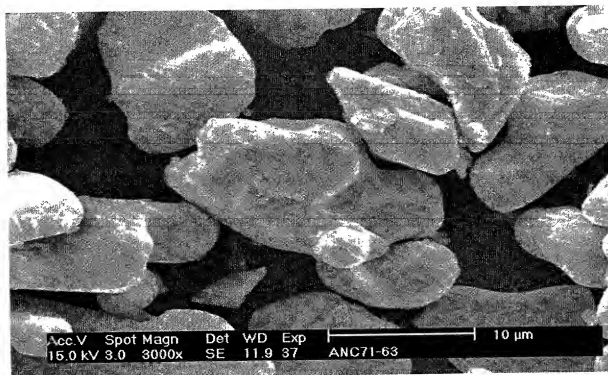
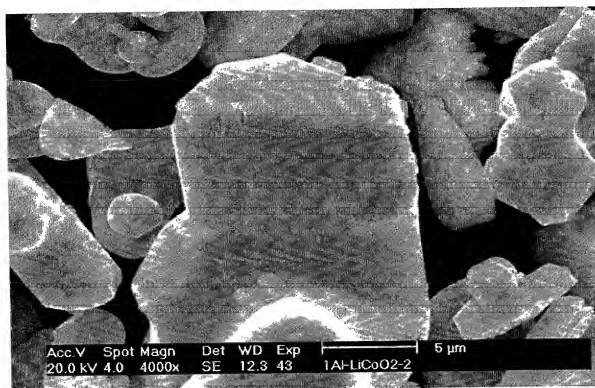


FIG. 28



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FIG. 29

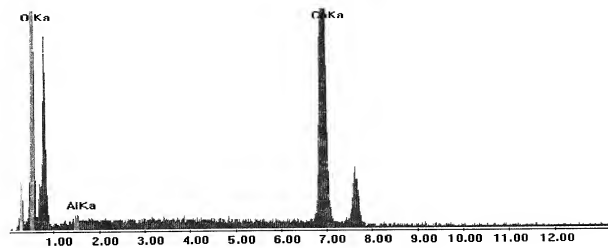
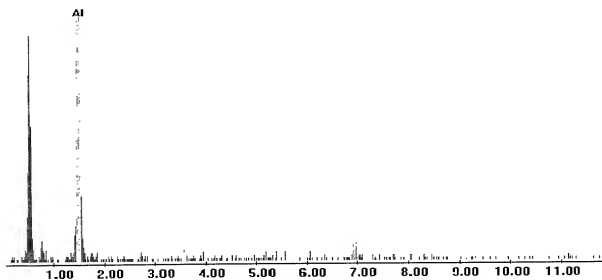


FIG. 30



# RED-LINED SUBSTITUTE SPECIFICATION

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**POSITIVE ACTIVE MATERIAL FOR POSITIVE-ELECTRODE USED IN  
LITHIUM SECONDARY RECHARGEABLE LITHIUM BATTERY AND  
METHOD OF MANUFACTURING PREPARING SAME**

**CROSS REFERENCE TO RELATED APPLICATION**

5        This application is a continuation application of pending prior United States Patent Application Serial No. 09/248,202, filed on February 10, 1999, which is incorporated by reference herein in its entirety. In addition, Korean Patent Application Nos. 98-3755, 98-12005, and 98-42956 filed on February 10, April 6, and October 14, 1998, and entitled: "Active material for positive  
10        electrode used in the lithium secondary battery and method of manufacturing the same," is incorporated by reference herein in its entirety.

**BACKGROUND OF THE INVENTION**

**(a) Field of the Invention**

15        The present invention relates to lithium secondary batteries. More particularly, the present invention relates to active material for a positive electrode used in lithium second batteries and a method of manufacturing the same in which structural and thermal stability of the active material are improved, thereby greatly enhancing the overall safety of the battery.

20        **(b) Description of the Related Art**

With the proliferation in the use of portable electronic devices in recent times, coupled with advancements made enabling increasingly smaller sizes and weights for these devices, research is being actively pursued to improve energy density capabilities of lithium secondary batteries.

25        Lithium secondary batteries utilize material that is able to undergo lithium ion intercalation and deintercalation respectively for a negative electrode and a positive electrode, and are filled with organic electrolyte or polymer electrolyte, which enable movement of lithium ions inside the battery (i.e., back to the negative electrode in the form of an ionic current). The lithium secondary  
30        battery generates electrical energy by processes of oxidation and reduction

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which take place when lithium ions undergo intercalation and deintercalation in the negative electrode and the positive electrode, respectively.

— In the past, although lithium metal was used as the negative electrode active material in lithium secondary batteries, a serious problem of dendrite forming on a surface of the lithium metal resulted during charging and discharging. This may cause a short circuit, or more seriously may lead to the explosion of the battery. To prevent such problems, carbonaceous material is now widely used for the negative active material. Carbonaceous material is able to alternately either receive or supply lithium ions while maintaining its structural integrity and electrical properties, and half of a potential of the cell is identical to that of lithium metal during insertion and separation of ions.

— For the active material of the positive electrode in secondary batteries, a metal chalcogenide compound, enabling insertion and separation of lithium ions, is generally used, i.e. composite metal oxides such as  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNiO}_2$ ,  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  ( $0 < x < 1$ ), and  $\text{LiMnO}_2$ . Regarding the advantages and disadvantages of these different materials: the Mn-based active materials,  $\text{LiMn}_2\text{O}_4$ , and  $\text{LiMnO}_2$ , can easily synthesize, are less expensive than the other materials and give minimal negative affects on the environment, but capacities of these materials are low;  $\text{LiCoO}_2$  is widely used as it exhibits an electrical conductivity of roughly  $10^{-2}$  to  $1 \text{ S/cm}$  at room temperature, provides a high level of battery voltage, and has exceptional electrode characteristics, but is unsafe when charging or discharging at a high rate, and is more costly than the other materials; and  $\text{LiNiO}_2$  has a high discharge and charge capacity and is the least expensive of the above active materials for the positive electrode, but does not synthesize easily.

— Generally, such composite metal oxides are manufactured by mixing with a solid raw material powder, and this mixture undergoes a solid phase reaction for providing plasticity to the mixture. For example, Japanese Laid-open Publication No. Heisei 8-153513 (Sony Corp.) discloses a method for manufacturing  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  ( $0 < x < 1$ ) in which after a hydroxide containing  $\text{Ni(OH)}_2$  and  $\text{Co(OH)}_2$  or Ni and Co is mixed and heat treated, the hydroxide is ground and fractionated to diameter sizes of the particles. In another method,  $\text{LiOH}$ , Ni oxide and Co oxide are reacted, and after undergoing a first sintering at  $400$  to  $580^\circ\text{C}$  to form an oxide, a second sintering is performed at  $600$  to



780°C to manufacture a perfect crystalline active material.

However, in such conventional methods, the resulting active material has a low degree of both structural and thermal stability, reducing the safety of the battery. **(a) Field of the Invention**

The present invention relates to a positive active material for a rechargeable lithium battery and a method of preparing the same, and more particularly, to a positive active material for a rechargeable lithium battery and a method of preparing the same in which the positive active material exhibits improved structural and thermal stability.

**(b) Description of the Related Art**

The use of portable electronic instruments is increasing as electronic equipment gets smaller and lighter due to developments in high-tech electronic industries. Studies on rechargeable lithium batteries are actively being pursued in accordance with the increased need for a battery having a high energy density for use as a power source in these portable electronic instruments.

Rechargeable lithium batteries use material into or from which lithium ions are reversibly intercalated or deintercalated as negative and positive active materials. For an electrolyte, an organic solvent or polymer is used. Rechargeable lithium batteries produce electrical energy from changes of chemical potentials of the active material during the intercalation and deintercalation reactions of lithium ions.

For the negative active material in a rechargeable lithium battery, metallic lithium was used in the early period of development. However, the lithium negative electrode degrades due to a chemical reaction with the electrolyte. Lithium dissolved in an electrolyte as lithium ions upon discharging is deposited as lithium metal on the negative electrode upon charging. When charge-discharge cycles are repeated, lithium is deposited in the form of dendrites which are more reactive toward the electrolyte due to an enhanced surface area, and they may also induce a short circuit between the negative and positive active materials and even cause an explosion of the battery in the worse case. Such problems have been addressed by replacing lithium metal with carbon-based materials such as an amorphous or crystalline carbon. The

carbon-based materials reversibly accept and donate significant amounts of lithium without affecting their mechanical and electrical properties, and the chemical potential of lithiated carbon-based material is almost identical to that of lithium metal.

5 For the positive active material in the rechargeable lithium battery, a metal chalcogenide compound into or from which lithium ions are intercalated or deintercalated is used. Typical examples include  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ ,  $\text{LiNiO}_2$ ,  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  ( $0 < x < 1$ ), or  $\text{LiMnO}_2$ . Mn-based active materials such as  $\text{LiMn}_2\text{O}_4$  or  $\text{LiMnO}_2$  are the easiest to prepare and they are less expensive and much  
10 more environmentally friendly than the other materials, but they have significantly smaller capacities than the other materials.  $\text{LiCoO}_2$  exhibits good electrical conductivity of  $10^{-2}$  to 1 S/cm at ambient temperatures, as well as high cell voltage and good electrochemical properties. Therefore, it is widely used in commercially available rechargeable lithium batteries, although the cobalt-based active material is relatively more expensive than the other  
15 materials.  $\text{LiNiO}_2$  has an advantage of having the highest specific capacity of all, but it is relatively more difficult to synthesize in the desired quality level and is the least stable of all.

These composite metal oxides are manufactured by a solid-phase method. The solid-phase method involves mixing solid raw material powders and sintering the mixture. For example, Japanese Patent publication No. Hei 8-153513 discloses a method in which  $\text{Ni(OH)}_2$  is mixed with  $\text{Co(OH)}_2$  or mixed hydroxides of Ni and Co are heat-treated, ground, and then sieved to produce  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$  ( $0 < x < 1$ ). In another method, a reactant mixture of  $\text{LiOH}$ , Ni  
20 oxide and Co oxide is initially heated at 400 to 580 , and then the heated reactant is heated again at 600 to 780 to produce a crystalline active material.

Another way to produce such composite metal oxides is disclosed in Japanese Patent Laid open Hei. 9-55210 (Sony). In this method, a Ni-based material is coated with a metal alkoxide to prepare a positive active material.  
25 The metal alkoxide includes Co, Al or Mn. However, the metal coatings in the Ni-based material did not show improvements in the cell performance, e.g. capacity and voltage.

In addition, U.S. Patent No. 5,705,291 (Bell Communications Research, Inc.) discloses that  $\text{LiMn}_2\text{O}_4$  is mixed with aluminum oxide and briefly heated to

obtain an active material with improved behavior. However, this material did not provide with a sufficient improvement in cell performances to satisfy commercial needs.

Therefore, there is sufficient need to develop positive active materials with improved structural and thermal stability, capacity, and cycle life.

### SUMMARY OF THE INVENTION

The present invention has been made in an effort to fulfill the above need.

It is an object of the present invention to provide active material for a positive electrode used in lithium secondary batteries in which the active material has a high degree of rechargeable lithium battery with improved structural and thermal stability, capacity and cycle life.

It is another object of the present invention to provide a method of manufacturing the preparing the positive active material having the above characteristics, for a rechargeable lithium battery.

To achieve the above objects, the present invention provides a positive active material for a rechargeable lithium battery including a core comprising at least one compound represented by Formula 1 and a protective active metal oxide shell formed on the core, the active metal oxide being positive electrode used in lithium secondary batteries of Formula 1 below in which capable of stabilizing a structure of the active material:

Formula 1

$\text{LiA}_{1-x}\text{yB}_x\text{C}_y\text{O}_2$ ,

where  $0 < x < 0.3$ , and  $0 < y < 0.01$ ;

A is an element selected from the group consisting of Co and Mn;

B is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al; and

C is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al.

The positive active material is obtained from a process of preparing crystalline powder or semi-crystalline powder of Formula 1 is manufactured, and after represented by Formula 1, coating the crystalline powder or semi-crystalline powder with metal alkoxide sol, the coated powder is heated,

thereby producing an active material that is coated with a metal oxide on its surface.

— [Formula 1]

—  $\text{LiA}_{1-x}\text{B}_x\text{C}_y\text{O}_2$

5 — where  $0 < x \leq 0.3$ , and  $0 \leq y \leq 0.01$ .

— In the Formula 1 above, A is an element selected from the group consisting of Ni, Co and Mn; B is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al; and C is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al.

10 or semi-crystalline powder with a metal alkoxide suspension, and heat-treating the coated powder.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

Further objects and other advantages of the present invention will become apparent from the following description in conjunction with the attached drawings, in which:

15 FIGs. 1a and 1b are SEM1A and 1B are scanning electronic microscope (SEM) pictures of a positive active material for a positive electrode used in secondary lithium batteries prepared according to a first example Example 1 of the present invention;

20 FIGs. 2a2A and 2b2B are SEM pictures of a positive active material for a positive electrode used in secondary lithium batteries prepared according to a first comparative example of the present invention; Comparative Example 1;

25 FIG. 3 is a graph illustrating XRD patterns of active material for a positive electrode used in secondary lithium batteries according to a second example and a second comparative example of the present invention; positive active materials prepared according to Example 2 (b) of the present invention, Comparative Example 2 (c), and semi-crystalline  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  (a);

30 FIG. 4 is a graph illustrating charge and discharge cycle-life characteristics of a battery to which is applied positive material according to the first example, the first comparative example and a third example of the present invention;

— FIGs. 5a and 5b are SEM pictures of active material for a positive

electrode used in secondary lithium batteries according to a fifth example and a third comparative example; cells prepared according to Example 1 (a) and Example 3 (b) of the present invention, and Comparative Example 1 (c);

FIGs. 5A and 5B are SEM pictures of positive active materials prepared according to Example 5 of the present invention and Comparative Example 3, respectively;

FIG. 6 is a graph illustrating XRD patterns of active material for a positive electrode used in secondary lithium batteries according to the fifth example, the third comparative example and a fourth comparative example of the present invention; positive active materials prepared according to Example 5 (A) of the present invention and Comparative Example 3 (B) and Comparative Examples 4 (C);

FIG. 7 is a graph illustrating charge and discharge cycle-life characteristics of a battery to which is applied positive material according to the fifth example and the third comparative example of the present invention; cells prepared according to Example 5 (a) of the present invention and Comparative Example 3 (b);

FIG. 8 is a graph illustrating DSC differential scanning calorimetry (DSC) analysis results of a positive plate to which is applied positive material according to a ninth example and a fifth comparative example of the present invention; positive electrodes prepared according to Example 9 (b) of the present invention and Comparative Example 5 (a);

FIG. 9 is a graph illustrating battery characteristics during charging and discharging at a level of voltage between 2.75V and 4.1V of a battery to which is applied positive material according to the ninth example and the fifth comparative example; cycle-life characteristics of cells prepared according to Example 9 (a) of the present invention and Comparative Example 5 (b) for charge and discharge in the voltage range of 4.1 to 2.75V;

FIG. 10 is a graph illustrating battery characteristics during charging and discharging at a level of voltage between 2.75V and 4.2V of a battery to which is applied positive material according to the ninth example and the fifth comparative example; cycle-life characteristics of cells prepared according to Example 9 (a) of the present invention and Comparative Example 5 (b) for charge and discharge in the voltage range of 4.2 to 2.75V;

FIG. 11 is a graph illustrating battery characteristics during charging and discharging at a level of voltage between 2.75V and 4.3V of a battery to which is applied positive material according to the ninth example and the fifth comparative example; cycle-life characteristics of cells prepared according to Example 9 (a) of the present invention and Comparative Example 5 (b) for charge and discharge in the voltage range of 4.3 to 2.75V;

FIG. 12 is a graph illustrating XRD patterns of active material for a positive electrode used in secondary lithium batteries according to a tenth example and the fifth comparative example of the present invention; positive active materials of Comparative Example 5 (a) before charging, and Example 10 (b) of the present invention after charging at 4.2V and Comparative Example 5 (c) after 1 cycle charging at 4.2V;

FIG. 13 is a graph illustrating DSC analysis results of a positive plate after charged to 4.2V to which is applied positive material according to the tenth example and the fifth comparative example of the present invention; positive electrodes after charging at 4.2V, prepared according to Example 10 (b) of the present invention and Comparative Example 5 (a);

FIG. 14 is a graph illustrating DSC analysis results of a positive plate after charged to 4.1V to which is applied positive material according to the tenth example and the fifth comparative example of the present invention; positive electrodes after charging at 4.1V, prepared according to Example 10 (b) of the present invention and Comparative Example 5 (a);

FIG. 15 is a graph illustrating DSC analysis results of a positive plate to which is applied positive material according to an eleventh example and a sixth comparative example of the present invention; positive electrodes after charging at 4.1V, prepared according to Example 11 (b) of the present invention and Comparative Example 6 (a);

FIG. 16 is a graph illustrating DSC analysis results of a positive plate to which is applied positive material according to a twelfth example and a seventh comparative example of the present invention; positive electrodes after charging at 4.3V, prepared according to Example 12 (b) of the present invention and Comparative Example 7 (a);

FIG. 17 is a graph illustrating DSC analysis results of a positive plate to which is applied positive material according to a thirteenth example and an

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eighth comparative example of the present invention; positive electrodes after charging at 4.3V, prepared according to Example 13 (b) of the present invention and Comparative Example 8 (a);

FIG. 18 is a ~~TEM~~transmission electronic microscopy (TEM) picture of a positive active material prepared according to a fourteenth exampleExample 14 of the present invention;

FIG. 19 is a TEM picture of a positive active material prepared according to a fifteenth exampleExample 15 of the present invention;

FIG. 20 is a graph illustrating a cycle life of a battery to which is applied active material according to a sixteenth example and a tenth comparative example of the present invention; characteristics of cells prepared according to Example 16 (a) of the present invention and Comparative Example 10 (b);

FIG. 21 is a graph illustrating charge and discharge charge-discharge characteristics of a battery to which is applied positive material cell prepared according to a ~~seventeenth example~~Example 17 of the present invention;

FIG. 22 is a graph illustrating charge and discharge charge-discharge characteristics of a battery to which is applied positive material according to an eleventh comparative example of the present invention; and cell with the positive active material prepared according to Comparative example 11.

FIG. 23 is a graph illustrating a cycle life of a battery to which is applied active material according to an eighteenth example and a twelfth comparative example of the present invention; cycle life characteristics of cells prepared according to Example 18 (open circles) of the present invention and Comparative Example 12 (filled circles);

#### **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

— The present invention relates to active material for a positive electrode used in lithium secondary batteries of Formula 1 below in which crystalline powder or semi-crystalline powder of Formula 1 is manufactured, and after coating the crystalline powder or semi-crystalline powder with metal alkoxide sol, the coated powder is heated, thereby producing an active material that is coated with a metal oxide on its surface.

— [Formula 1]

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——  $\text{LiA}_{1-x}\text{B}_x\text{C}_y\text{O}_2$

—— where  $0 < x \leq 0.3$ , and  $0 \leq y \leq 0.01$ .

—— In the Formula 1 above, A is an element selected from the group consisting of Ni, Co and Mn; B is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al; and C is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al.

—— To synthesize a crystalline or a semi-crystalline powder of  $\text{LiA}_{1-x}\text{B}_x\text{C}_y\text{O}_2$  (where  $0 < x \leq 0.3$ ;  $0 \leq y \leq 0.01$ ; A is an element selected from the group consisting of Ni, Co and Mn; B is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al; and C is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al), a uniform mixture of an A, B, C metal salt is produced by mixing metal A with metal B to an equivalent ratio between 70:30 and 100:0; and a small amount of metal C is added to the mixture. Here, it is possible for metal C to not be added to the mixture. With regard to the ratio between metal A and metal B, if an equivalent ratio of metal B exceeds 30%, as changes occur in a crystalline structure of the resulting positive electrode active material, lithium ion intercalation and deintercalation are not smoothly realized.

—— In order to uniformly mix the A, B, C metal salt powder, it is preferable that the A, B, C salt is evenly dispersed in a suitable solvent such that a mixed solution is produced, and that the mixed solution undergoes an attritor milling process. For the solvent, it is possible to use water, alcohol or acetone, and it is preferable that the above metal salts are not dissolved in the solvent. Attritor milling refers to agitating (the A, B, C metal salt dispersed in the solvent in this case) using an agitator. Here, a sufficient speed and agitation time (e.g., 400 to 500 rpm for roughly 1 hour) is used to ensure the metal salt powder is uniformly mixed.

—— It is preferable to use nickel salt such as nickel hydroxide, nickel nitrite, or nickel acetate for the A metal salt; for the B metal salt, it is preferable to use cobalt salt such as cobalt hydroxide, cobalt nitride or cobalt carbonate; and for the C metal salt it is preferable to use aluminum hydroxide or strontium hydroxide.

—— After drying the solvent, in which the mixed powder is uniformly



dispersed, in a drying furnace at a temperature of approximately  $120^{\circ}\text{C}$  for roughly 24 hours, the resulting material is neatly ground, thereby producing a  $\text{A}_{1-x}\text{yB}_x\text{C}_y\text{O}_2(\text{OH})_2$  powder. A lithium salt is added to the produced powder at a desired equivalent ratio and mechanically mixed therein. For example, the mixture of the lithium salt and  $\text{A}_{1-x}\text{yB}_x\text{C}_y\text{O}_2(\text{OH})_2$  is produced by performing a mortar-grinder mixing operation.

For the lithium salt, although any chemical can be used which reacts with  $\text{A}_{1-x}\text{yB}_x\text{C}_y\text{O}_2(\text{OH})_2$ , it is preferable to use lithium nitrite, lithium acetate or lithium hydroxide. At this time, to accelerate the reaction between the lithium salt and  $\text{A}_{1-x}\text{yB}_x\text{C}_y\text{O}_2(\text{OH})_2$ , it is preferable that a suitable solvent such as ethanol, methanol, water or acetone is added, and the mortar-grinder mixing operation is performed until the mixture is solvent-free.

The mixture of the lithium salt and  $\text{A}_{1-x}\text{yB}_x\text{C}_y\text{O}_2(\text{OH})_2$  produced by the above process is heat-treated at a temperature between  $400$  and  $600^{\circ}\text{C}$ , thereby producing a  $\text{LiA}_{1-x}\text{yB}_x\text{C}_y\text{O}_2$  powder (i.e., an active material precursor for positive electrodes), the powder being in a semi-crystalline state.

In another method, the mixture of the produced lithium salt and  $\text{A}_{1-x}\text{yB}_x\text{C}_y\text{O}_2(\text{OH})_2$  undergoes a first heat treating process for 1-5 hours at a temperature between  $400$  and  $550^{\circ}\text{C}$ , and a second heat treating process for 10-15 hours at a temperature between  $700$  and  $900^{\circ}\text{C}$ , thereby producing a  $\text{LiA}_{1-x}\text{yB}_x\text{C}_y\text{O}_2$  powder (i.e., an active material precursor for a positive electrode), the powder being in a crystalline state. If the temperature is below  $400^{\circ}\text{C}$  for the first heat treating process, a sufficient level of reaction with the lithium salt is not realized, and if the temperature is below  $700^{\circ}\text{C}$  for the second heat treating process, it is difficult to form the crystalline material of Formula 1. Further, the first and second heat treating processes are performed in a state where air is being blown and the temperature is increased at a rate of  $1-5^{\circ}\text{C}/\text{minute}$ . After heat treating for the lengths of times described above, the mixture is naturally cooled. Preferably, the crystalline or semi-crystalline  $\text{LiA}_{1-x}\text{yB}_x\text{C}_y\text{O}_2$  powder is remixed at a high temperature so that a more uniform mixing of the lithium salt is attained.

Subsequently, the crystalline or semi-crystalline  $\text{LiA}_{1-x}\text{yB}_x\text{C}_y\text{O}_2$  powder is coated with metal alkoxide sol. At this time, it is preferable that a dip coating method is used as it is simple to execute, although it is possible to use other

typically applied methods such as a sputtering method or a CVD (chemical vapor deposition) method. The metal alkoxide sol is produced by mixing metal with alcohol at 1-10% by weight of the alcohol, then refluxing the mixture. Mg, Al, Co, K, Na or Ca, preferably Mg, is used for the metal in the metal alkoxide sol; and either methanol or ethanol can be used for the alcohol in the mixture. If a concentration of the metal is less than 1% by weight, advantageous effects of coating the metal alkoxide sol on the  $\text{LiA}_{1-x-y}\text{B}_x\text{C}_y\text{O}_2$  powder are not obtained, while if the concentration of the metal exceeds 5% by weight, a layer formed by the metal alkoxide sol on the powder becomes too thick.

Following the above, the crystalline or semi-crystalline powder coated with metal alkoxide sol is dried in an oven set at  $120^\circ\text{C}$  for roughly 5 hours. This drying process acts to more uniformly disperse the lithium salt in the powder. Next, the crystalline or semi-crystalline  $\text{LiA}_{1-x-y}\text{B}_x\text{C}_y\text{O}_2$  powder coated with metal alkoxide sol is heat-treated for 8-15 hours at a temperature between  $400$  and  $900^\circ\text{C}$ . That is, in the case where the powder is crystalline, it is preferable that the heat-treating temperature is set between  $400$  and  $600^\circ\text{C}$ , whereas the preferable temperature is between  $700$  and  $900^\circ\text{C}$  in the case where the powder is semi-crystalline.

By the above heat-treating process, the metal alkoxide sol changes to a metal oxide, and the semi-crystalline  $\text{LiA}_{1-x-y}\text{B}_x\text{C}_y\text{O}_2$  powder changes to a crystalline powder, resulting in the production of positive electrode active material of Formula 1 in which metal oxide is coated on a surface of a crystalline  $\text{LiA}_{1-x-y}\text{B}_x\text{C}_y\text{O}_2$  powder. The metal oxide formed on the surface of the active material can be either a composite metal oxide obtained from at least one of the A, B or C metals and the metal alkoxide, or a metal oxide obtained from only the metal alkoxide. For example, by heat-treating  $\text{LiCoO}_2$  after coating the same with aluminum alkoxide, a positive electrode active material of a composite metal oxide of cobalt and aluminum, and/or a positive electrode active material on a surface of which aluminum oxide is processed can be obtained. To produce a more uniform crystalline active material, it is preferable for dry air or oxygen to be blown during the heat-treating process. At this time, if the heat-treating temperature is below  $400^\circ\text{C}$ , since the coated metal alkoxide sol does not become crystallized, use of the resulting active material in a battery causes interference of movement of lithium ions therein.

— In the positive electrode active material produced as in the above, since minute particles are in an agglomerated state, particle size of the active material is between 0.1 and 100  $\mu\text{m}$ . FIG. 24 is a graph illustrating the charge

and discharge characteristics of the positive active materials according to Example 19 (B) of the present invention and Comparative example 13 (A); and

FIG. 25 is a graph illustrating XRD results of a synthesized  $\text{Al}_2\text{O}_3$  (B) and a commercial  $\text{Al}_2\text{O}_3$  (A);

FIG. 26 is a graph illustrating the charge and discharge characteristics of the coin-type half-cells containing  $\text{LiCoO}_2$  (A) and  $\text{LiCoO}_2$  coated with  $\text{Al}_2\text{O}_3$  (B) and  $\text{LiCoO}_2$  coated with a commercial  $\text{Al}_2\text{O}_3$  (C);

FIG. 27 is a SEM picture of a positive active material according to Example 21 of the present invention;

FIG. 28 is a SEM picture of a positive active material according to Comparative example 15;

FIG. 29 is a graph illustrating an EDX result of a positive active material according to Example 21 of the present invention; and

FIG. 30 is a graph illustrating an EDX result of a positive active material according to Comparative example 15.

### **DETAILED DESCRIPTION OF THE INVENTION**

A positive active material of the present invention includes a core including at least one compound represented by Formula 1 and a protective active metal oxide shell formed on the core:

Formula 1

$\text{LiA}_{1-x-y}\text{B}_x\text{C}_y\text{O}_2$

where  $0 < x < 0.3$ , and  $0 < y < 0.01$ ;

A is an element selected from the group consisting of Co and Mn;

B is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al; and

C is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al.

The core preferably includes  $\text{LiCoO}_2$ , and a metal in the active metal oxide includes Mg, Al, Co, K, Na or Ca, and preferably Al. Thus, the preferred metal oxide is active  $\text{Al}_2\text{O}_3$ . The active metal oxide has an amorphous phase.

The metal oxide is capable of stabilizing the active material.

A method of preparing the positive active material will be illustrated in more detail.

An A-metal salt is mixed with a B-metal salt in an equivalence ratio of between 70:30 and 100:0. Alternatively, a trace amount of a C-metal salt may be added to the mixture. If the B-metal salt is present over 30% of the sum of A- and B-metal salts, intercalation and deintercalation reactions of lithium ions do not proceed without changes in a crystalline structure of the resulting positive active material.

The mixing procedure is preferably performed by dispersing the A-, B- and C-metal salts in a suitable solvent and milling the resulting suspension by using an attritor. Although the solvent may be any solvent in which the A-, B- and C-metal salts are not soluble, preferable examples include water, an alcohol or acetone. Here, the milling is performed at a sufficiently high rate for a sufficient period of time to allow uniform mixing, for example, 400 to 500 rpm for about 1 hour.

For example, a nickel salt such as nickel hydroxide, nickel nitrate, or nickel acetate may be used for the A-metal salt; for the B-metal salt, a cobalt salt such as cobalt hydroxide, cobalt nitrate or cobalt carbonate may be used; and for the C-metal salt, aluminum hydroxide or strontium hydroxide may be used.

The resulting suspension is dried in a drying furnace at about 120 °C for 24 hours and the dried material is ground to prepare an  $A_{1-x-y}B_xC_y(OH)_2$  ( $0 \leq x \leq 0.3$ ,  $0 \leq y \leq 0.01$ ) powder. A lithium salt is added to the produced powder in a desired equivalence ratio and mechanically mixed. For example, the mixture of the lithium salt and  $A_{1-x-y}B_xC_y(OH)_2$  is produced by mixing them in a mortar or grinder.

For the lithium salt, although any one of many simple lithium salts that react with  $A_{1-x-y}B_xC_y(OH)_2$  may be used, it is preferable to use lithium nitrate, lithium acetate or lithium hydroxide. In order to facilitate the reaction between the lithium salt and  $A_{1-x-y}B_xC_y(OH)_2$ , it is preferable that a suitable solvent such as ethanol, methanol, water or acetone is added, and then the mixture is mixed well by grinding in a mortar until excess liquid solvent disappears from the mixture.

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The mixture of the lithium salt and  $A_{1-x-y}B_xC_y(OH)_2$  is heat-treated at a temperature between 400 and 600 , thereby producing a crystalline or semi-crystalline, positive active material precursor  $LiA_{1-x-y}B_xC_yO_2$  powder.

Alternatively, the mixture of the lithium salt and  $A_{1-x-y}B_xC_y(OH)_2$  is heat-treated for 1 to 5 hours at a temperature between 400 and 550 (first heat-treatment), and the resulting material is again heat-treated for 10 to 15 hours at a temperature between 700 and 900 (second heat-treatment), thereby producing a crystalline or a semi-crystalline positive active material precursor  $LiA_{1-x-y}B_xC_yO_2$  powder. If the first heat-treatment temperature is below 400 , the metal salts do not react completely with the lithium salts, and if the second heat-treatment temperature is below 700 , it is difficult to form the crystalline or the semi-crystalline material of Formula 1. The first and second heat-treatments are performed by increasing the temperature at a rate of 1 to 5 /min in a stream of air. The mixture is cooled slowly after turning off the heating source. Preferably, the  $LiA_{1-x-y}B_xC_yO_2$  powder is then reground to distribute the lithium salts uniformly.

Subsequently, the crystalline or semi-crystalline  $LiA_{1-x-y}B_xC_yO_2$  powder is coated with a metal alkoxide suspension. The coating process may be performed by dip-coating or by using any other general-purpose coating technique. Alternatively, the coating may also be achieved by a sputtering method, a chemical vapor deposition (CVD) method. Any other coating techniques, if available and applicable, may be as effective as the methods described herein, but it is preferable to use a dip-coating method using a metal alkoxide suspension since it is simple to use and economical.

The metal alkoxide suspension is prepared by mixing the metal or metal alkoxide powder with an alcohol at 1 to 10% by weight of the alcohol, preferably followed by refluxing the mixture. The metal of the metal alkoxide may be Mg, Al, Co, K, Na or Ca, preferably Al, and the alcohol may be methanol, ethanol or isopropanol. For the dip-coating process, if the concentration of the metal is less than 1% by weight, advantageous effects of coating the  $LiA_{1-x-y}B_xC_yO_2$  powder with the metal alkoxide suspension are not sufficient, while if the concentration of the metal exceeds 10% by weight, the coating layer formed by the metal alkoxide suspension on the powder becomes too thick.

After dip-coating the crystalline or semi-crystalline powder with the alkoxide suspension, the wet powder is dried in an oven at 120 for about 5 hours. This drying step is performed to distribute lithium salt uniformly in the powder. The dried crystalline  $\text{LiA}_{1-x-y}\text{B}_x\text{C}_y\text{O}_2$  powder with coating layer is heat-treated for 8 to 15 hours at a temperature between 400 and 900. In the case where the powder is crystalline, it is preferable that the heat-treating temperature is set between 400 and 600, whereas the preferable temperature is between 700 and 900 in the case where the powder is semi-crystalline.

By the heat-treating process, the metal alkoxide suspension is converted to metal oxide, and the semi-crystalline  $\text{LiA}_{1-x-y}\text{B}_x\text{C}_y\text{O}_2$  powder is converted to a crystalline powder, resulting in the production of positive active material of Formula 1 in which metal oxide is coated on a surface of a crystalline  $\text{LiA}_{1-x-y}\text{B}_x\text{C}_y\text{O}_2$  powder. The metal oxide formed on the surface of the active material can be either a composite metal oxide obtained from at least one of the A-, B- or C- metals and the metal alkoxide, or a metal oxide obtained from only the metal alkoxide. For example, by heat-treating  $\text{LiCoO}_2$  coated with aluminum alkoxide, a positive active material of a composite metal oxide of cobalt and aluminum, and/or a positive active material with a surface on which aluminum oxide is coated, can be obtained. To produce a more uniform crystalline active material, it is preferable to dry in air or oxygen by blowing it thereon during the heat-treating process. If the heat-treating temperature is below 400, since the coated metal alkoxide suspension does not become crystallized, the resulting active material does not give good performance in a battery since the movement of lithium ions therein is hindered.

The resulting positive active material prepared by the process described above is made of agglomerated minute particles, the particle size being between 0.1 and 100.

The present invention will now be described in detail following examples further illustrate the present invention.

(Example 1)

$\text{Ni}(\text{OH})_2$  powder (Tanaka Co. of Japan) and  $\text{Co}(\text{OH})_2$  (Kojyundo Chemical of Japan) powder were mixed to an equivalent ratio of 0.8/0.2 in an equivalence ratio of 0.8/0.2 and dispersed in water, after which the mixture

underwent an attritor milling process for approximately 60 minutes at 450 rpm to uniformly mix the mixture, and the resulting material was mixed and milled by using an attritor for 60 minutes at 450 rpm. The resulting mixture was dried in a drying oven at 120 °C for about 24 hours, and the Next, after drying the mixed powder dispersed in water in a drying oven at 120 °C for approximately 24 hours, the resulting dry mixture was evenly ground, thereby producing  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$ . LiOH (Junsei Co. of Japan) was added to the  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$  to provide 1 equivalent weight of lithium and the mixture underwent mortar grinder mixing such that a  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$  mixture was produced. dried mixture having a composition of  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$  was evenly ground. To this powder, a stoichiometric amount of LiOH was added, followed by grinding the resultant powder mixture in a mortar to achieve an even blend.

After the above, the The resultant powder mixture was heat-treated at 500 °C for approximately 5 hours, thereby producing a  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder. 500 for about 5 hours to obtain a semi-crystalline powder of  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ . The semi-crystalline  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder was then dip-coated in with a Mg-methoxide sol, produced suspension. The Mg-methoxide suspension was prepared by refluxing Mg powder of 4% by weight of methanol, after which the Mg-methoxide methanol. The coated semi-crystalline powder was remixed at a high temperature in a state where dry air was being blown thereon. Accordingly, the stream of dry air to distribute lithium salt was uniformly dispersed uniformly. The resulting material was then heat-treated for 12 hours at 750 °C in a state where dry air was blown thereon, 750 in a stream of dry air to obtain a coated crystalline positive active thereby producing crystalline active material for a positive electrode used in lithium secondary batteries. -material.

The active material manufactured as in the above, conductive material (carbon, product name: Super-P), positive active material, a conductive agent (carbon), a binder (polyvinylidene fluoride, product name: KF-1300) and a solvent (N-methyl pyrrolidone) were mixed to produce an prepare a positive active material composite slurry for a positive electrode slurry. The slurry was then cast into a tape shape on an Al foil current collector to manufacture a positive electrode. Using this positive electrode, Li metal as a counterpart

electrode, a Li-metal counter electrode, a sheet of microporous polypropylene separator, and an electrolyte including both a solution of 1M LiPF<sub>6</sub> in a 1:1 volume mixture of ethylene carbonate (EC) and dimethyl carbonate at a 1:1 volume ratio, and LiPF<sub>6</sub>, a coin-cell-type half cell was manufactured. (DMC), a coin-type half-cell was fabricated.

(Example 2)

Except for adding ethanol to accelerate a coin-type half-cell was fabricated by the same procedure as in Example 1, except that acetone was added to the mixture of the lithium salt and Ni<sub>0.8</sub>Co<sub>0.2</sub>(OH)<sub>2</sub> in order to facilitate the reaction between LiOH and Ni<sub>0.8</sub>Co<sub>0.2</sub>(OH)<sub>2</sub> and performing mortar-grinder mixing until nearly all the acetone was no longer present in the mixture (a solvent-free state), the same method as that used in Example 1 above was used to produce Ni<sub>0.8</sub>Co<sub>0.2</sub>(OH)<sub>2</sub>, and mortar/grinder mixing was performed until liquid acetone positive electrode active material for a lithium secondary battery and to manufacture a coin-cell-type half cell disappeared from the mixture, instead of dry grinding as in Example 1.

(Example 3)

After producing a coin-type half-cell was fabricated by the same procedure in Example 1, except that a mixture of lithium salt and Ni<sub>0.8</sub>Co<sub>0.2</sub>(OH)<sub>2</sub>, except for heat-treating the mixture for approximately five hours at 600°C, Ni<sub>0.8</sub>Co<sub>0.2</sub>(OH)<sub>2</sub> was heat-treated for about five hours at 600 instead of 500 as in Example 1, to produce a semi-crystalline LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> powder, the same method as that used in Example 1 above was used to produce positive electrode active powder material for a lithium secondary battery and to manufacture a coin-cell-type half cell.

(Example 4)

After producing a coin-type half-cell was fabricated by the same procedure in Example 2, except that a mixture of lithium salt and Ni<sub>0.8</sub>Co<sub>0.2</sub>(OH)<sub>2</sub>, except for heat-treating the mixture for approximately Ni<sub>0.8</sub>Co<sub>0.2</sub>(OH)<sub>2</sub> was heat-treated for about five hours at 600°C, to produce a semi-crystalline LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> powder, the same method as that used in Example 2 above was used to produce positive



electrode-active powder.

material for a lithium secondary battery and to manufacture a coin cell type half cell.

(Example 5)

5 ———  $\text{Ni}(\text{OH})_2$  (Tanaka Co. of Japan) and  $\text{Co}(\text{OH})_2$  (Kojyundo Chemical of Japan) were mixed to an equivalent ratio of 0.8/0.2 and dispersed in water, after which the mixture underwent an attritor milling process for approximately 60 minutes at 450 rpm to uniformly mix the mixture. Next, after drying the mixed powder dispersed  $\text{Ni}(\text{OH})_2$  and  $\text{Co}(\text{OH})_2$  were mixed in an  
10 equivalence ratio of 0.8:0.2 and dispersed in water. The resulting mixture was mixed well by milling with an attritor for about 60 minutes at 450 rpm. The mixed powder was dried in water in a drying oven at 120°C for approximately 24 hours,  
15 120 for about 24 hours and the resulting dry mixture was evenly ground, thereby producing  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$ .  $\text{LiOH}$  (Junsei Co. of Japan) was added to the  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$  to provide 1 equivalent weight of lithium, and ethanol was added to accelerate/facilitate a reaction between the  $\text{LiOH}$  and  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$ , after which the mixture underwent mortar grinder mixing until almost all the ethanol was no longer present in the mixture.  
20  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$  and the mixture was mortar/grinder mixed until liquid ethanol disappeared from the mixture.

After the above, the fully mixed ~~Thereafter, the~~ mixture was placed in an aluminous alumina crucible and heat-treated at 400°C in a state where dry air was blown on the mixture, then again 400 in a stream of dry air, and then heat-treated again for 12 hours at 750°C-750 . In both the heat-treating processes,  
25 the temperature was raised at a rate of 3°C/min., 3 /min. The mixture was allowed to stand at the first and after reaching the target temperatures (400°C and 750°C) and maintaining this state for a predetermined time, the mixture was naturally second heat-treating temperatures for predetermined times, and the mixture was slowly cooled to produce a  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder.

30 The  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder ~~produced as in the above~~ was then dipped in Mg-methoxide sol for approximately 10 minutes, then removed from the sol solution. a Mg-methoxide suspension for about 10 minutes and the coated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder was then separated from the suspension. Subsequently,

the powder was dried in an oven set at 120°C for approximately at 120 for about 5 hours, thereby producing  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder coated with the Mg-methoxide. The powder was then heat-treated at a temperature of 500°C for approximately 10 hours in a state where dry air was blown on the powder, thereby completing the production of the active material for positive electrodes used in lithium secondary batteries. 500 for about 10 hours in a stream of dry air, thereby producing a positive active material.

Using the positive electrode active material manufactured as in the above, a coin-cell-type half-cell was manufactured active material, a coin-type half-cell was fabricated according to the method used in Example 1.

(Example 6)

Except for mixing  $\text{Ni}(\text{OH})_2$  (Tanaka Co. of Japan) and  $\text{Co}(\text{OH})_2$  (Kojyundo Chemical of Japan) to an equivalent ratio of 0.9/0.1 to result in positive electrode A coin-type half-cell was fabricated by the same procedure in Example 5 except that  $\text{Ni}(\text{OH})_2$  was mixed with  $\text{Co}(\text{OH})_2$  in an equivalence ratio of 0.9:0.1, thereby producing a positive active material having a formula of  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$ , the same method as that used in Example 5 above was used to manufacture a half  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  cell.

(Example 7)

Except for heat treating the A coin-type half-cell was fabricated by the same procedure as in Example 5 except that the Mg-methoxide coated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder at 600°C, the same method as that used in Example 5 above was used to manufacture positive electrode active material and a half cell. was heat-treated at 600 .

(Example 8)

Except for heat treating the A coin-type half-cell was fabricated by the same procedure as in Example 6 except that the Mg-methoxide coated  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  powder at 600°C, the same method as that used in Example 6 above was used to manufacture positive electrode active material and a half cell. was heat-treated at 600 .

(Example 9)

$\text{LiOH}$  (Junsei Co. of Japan) and  $\text{Co}(\text{OH})_2$  (Kojyundo Chemical of Japan)

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were mixed to in a 1:1 mole ratio. After adding an A sufficient amount of ethanol  
to this mixture sufficient to induce thorough reaction of the two chemicals, was  
added to the mixture to fabricate the reaction, and the mixture was mixed in a  
mechanical mortar mixer for approximately 4 about 1 hour until liquid solvent  
disappeared from the mixture.

hour, or until nearly all the solvent was no longer present in the powder mixture.

Next, the fully mixed The mixed powder was placed in an aluminous  
crucible and heat-treated for 5 hours at  $400^{\circ}\text{C}$  in a state where dry air was  
blown on the mixture, then again 400 in a stream of dry air, then heat-treated  
again for 12 hours at  $750^{\circ}\text{C}$ . 750 In both the heat-treating processes, the  
temperature was raised at a rate of  $3^{\circ}\text{C}/\text{min}$ , and  $3^{\circ}\text{C}/\text{min}$ . The mixture was  
allowed to stand at the first after reaching the target temperatures ( $400^{\circ}\text{C}$  and  
 $750^{\circ}\text{C}$ ) and maintaining this state for a predetermined time, the mixture was  
naturally cooled to produce a crystalline and the second heat-treating  
temperatures for predetermined period of time and was slowly cooled to  
produce a  $\text{LiCoO}_2$  powder.

The  $\text{LiCoO}_2$  powder produced as in the above was then dipped in Mg-  
methoxide sol for approximately 10 minutes, then removed from the sol  
solution a Mg-methoxide suspension for about 10 minutes, and the coated  
 $\text{LiCoO}_2$  powder was then separated from the suspension. Subsequently, the  
powder was dried in an oven set at  $120^{\circ}\text{C}$  for approximately at  $120^{\circ}\text{C}$  for about 5  
hours, thereby producing  $\text{LiCoO}_2$  powder coated with the Mg-methoxide. The  
powder was then heat-treated at a temperature of  $600^{\circ}\text{C}$  for approximately 40  
hours in a state where dry air was blown on the powder, thereby completing the  
production of the active material for positive electrodes used in lithium  
secondary batteries. 600 for about 10 hours in a stream of dry air, thereby  
producing a positive active material.

Using the positive electrode active material manufactured as in the  
above, a coin cell type half-cell was manufactured according to active material,  
a coin-type half-cell was fabricated according by the method used in Example  
1.

(Example 10)

Except for heat-treating the  $\text{LiCoO}_2$  powder coated with the Mg-

methoxide at a temperature of 700°C, the same method as that used in Example 9 above was used to manufacture positive electrode active material and a half-cell. A coin-type half-cell was fabricated by the same procedure as in Example 9 except that the Mg-methoxide coated  $\text{LiCoO}_2$  powder was heat-treated at a temperature of 700°C.

(Example 11)

Except for heat treating the coin-type half-cell was fabricated by the same procedure as in Example 5 except that the Mg-methoxide coated  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder coated with the Mg-methoxide was heat-treated at a temperature of 700°C, the same method as that used in Example 5 above was used to manufacture positive electrode active material and a half-cell. 700°C.

(Example 12)

$\text{Ni}(\text{OH})_2$  (Tanaka Co. of Japan),  $\text{Co}(\text{OH})_2$  (Kojyundo Chemical of Japan),  $\text{Ni}(\text{OH})_2$ ,  $\text{Co}(\text{OH})_2$ , and  $\text{Al}(\text{OH})_3$  were mixed to an equivalent ratio of 0.8/0.15/0.05 and dispersed in water, after which the mixture underwent an attritor milling process for approximately 60 minutes at 450 rpm to uniformly mix the mixture. Next, after drying the mixed powder dispersed in water in a drying oven at 120°C for approximately 24 hours, in an equivalence ratio of 0.8/0.15/0.05 and dispersed in water. The resulting mixture was mixed well by milling with an attritor for about 60 minutes at 450 rpm. The mixed powder was dried in a drying oven at 120°C for about 24 hours and the resulting dry mixture was evenly ground, thereby producing  $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}(\text{OH})_2$ .  $\text{LiOH}$  (Junsei Co. of Japan) was added to the  $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}(\text{OH})_2$  to provide make 1 equivalent of lithium per formula weight of lithium, the hydroxide, and ethanol was added to accelerate facilitate the reaction between the  $\text{LiOH}$  and  $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}(\text{OH})_2$ , after which the mixture underwent mortar grinder mixing until almost all the ethanol was no longer present in the mixture (i.e., until the mixture was solvent-free).  $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}(\text{OH})_2$ . The mixture was mixed in a mortar until liquid ethanol disappeared from the mixture.

After the above, the fully mixed The mixed mixture was placed in an aluminous alumina crucible and heat-treated at 400°C in a state where dry air was blown on the mixture, then again heat-treated for 12 hours at 750°C. In

both the 400 in a stream of dry air, then heat-treated again for 12 hours at 750. In both heat-treating processes, the temperature was raised at a rate of 3°C/min., and 3 /min. The mixture was allowed to stand at the first and the second after reaching the target temperatures (400°C and 750°C) and maintaining this state for a predetermined time, the mixture was naturally cooled to produce a  $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}(\text{OH})_2$  heat-treating temperatures for predetermined period of time and was slowly cooled to produce a  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powder.

The  $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}(\text{OH})_2$  powder produced as in the above was then dipped in Mg-methoxide sol for approximately 10 minutes, then removed from the sol solution.  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powder was then dipped in a Mg-methoxide suspension for about 10 minutes and the coated  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powder was then separated from the suspension. Subsequently, the powder was dried in an oven set at 120°C for approximately at 120 for about 5 hours, thereby producing  $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}(\text{OH})_2\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powder coated with the Mg-methoxide. The powder was then heat-treated at a temperature of 700°C for approximately 10 hours in a state where dry air was blown on the powder, thereby completing the production of the active material for positive electrodes used in lithium 700 for about 10 hours in a stream of dry air, thereby producing a positive active material.

secondary batteries.

Using the positive electrode active material manufactured as in the above, a coin-cell type half-cell active material, a coin-type half-cell was manufactured according to the method used in Example 1.

(Example 13)

$\text{Ni}(\text{OH})_2$  (Tanaka Co. of Japan),  $\text{Co}(\text{OH})_2$  (Kojyundo Chemical of Japan),  $\text{Ni}(\text{OH})_2$ ,  $\text{Co}(\text{OH})_2$ , and  $\text{Sr}(\text{OH})_2$  were mixed to an equivalent ratio of 0.9/0.0985/0.002 and dispersed in water, after which the mixture underwent an attritor milling process for approximately 60 minutes at 450 rpm to uniformly mix the mixture. Next, after drying the mixed powder dispersed in water in a drying oven at 120°C for approximately 24 hours in an equivalence ratio of 0.9/0.098:0.002 and dispersed in water. The resulting mixture was mixed well by milling with an attritor for about 60 minutes at 450 rpm. The mixed powder

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was dried in a drying oven at 120 for about 24 hours, and the resulting dry mixture was evenly ground, thereby producing  $\text{Ni}_{0.9}\text{Co}_{0.098}\text{Sr}_{0.002}(\text{OH})_2$ . LiOH (Junsei Co. of Japan) was added to the  $\text{Ni}_{0.9}\text{Co}_{0.098}\text{Sr}_{0.002}(\text{OH})_2$  to provide 1 equivalent weight of lithium, and ethanol was added to accelerate/facilitate a reaction between the LiOH and  $\text{Ni}_{0.9}\text{Co}_{0.098}\text{Sr}_{0.002}(\text{OH})_2$ , after which the mixture underwent mortar-grinder mixing until almost all the ethanol was no longer present in the mixture (i.e., until the mixture was solvent-free).  
5  $\text{Ni}_{0.9}\text{Co}_{0.098}\text{Sr}_{0.002}(\text{OH})_2$ . The mixture was mixed in a mortar until liquid ethanol disappeared from the mixture.

10 After the above, the fully-mixed/Thereafter, the mixed mixture was placed in an aluminous/alumina crucible and heat-treated at  $400^\circ\text{C}$  in a state where dry air was blown on the mixture, then again/400 in a stream of dry air, then heat-treated again for 12 hours at  $750^\circ\text{C}$ -750. In both the heat-treating processes, the temperature was raised at a rate of  $3^\circ\text{C}/\text{min}$ -3 /min. The mixture was allowed to stand at the first and after reaching the target temperatures ( $400^\circ\text{C}$  and  $750^\circ\text{C}$ ) and maintaining this state for a predetermined time, the mixture was naturally cooled to produce a  $\text{Ni}_{0.9}\text{Co}_{0.098}\text{Sr}_{0.002}(\text{OH})_2$ ; the second heat-treating temperatures for predetermined period of time, and the mixture was slowly cooled to produce a crystalline  $\text{LiNi}_{0.9}\text{Co}_{0.098}\text{Sr}_{0.002}\text{O}_2$  powder.  
15  
20

The  $\text{Ni}_{0.9}\text{Co}_{0.098}\text{Sr}_{0.002}(\text{OH})_2$  powder produced as in the above was then dipped in Mg methoxide sol for approximately 10 minutes, then removed from the sol solution.  $\text{LiNi}_{0.9}\text{Co}_{0.098}\text{Sr}_{0.002}\text{O}_2$  powder was then dipped in a Mg-methoxide suspension for about 10 minutes and the coated  
25  $\text{LiNi}_{0.9}\text{Co}_{0.098}\text{Sr}_{0.002}\text{O}_2$  powder was then separated from the suspension. Subsequently, the powder was dried in an oven set at  $120^\circ\text{C}$  for approximately at 120 for about 5 hours, thereby producing  $\text{Ni}_{0.9}\text{Co}_{0.098}\text{Sr}_{0.002}(\text{OH})_2$   $\text{LiNi}_{0.9}\text{Co}_{0.098}\text{Sr}_{0.002}\text{O}_2$  powder coated with the Mg-methoxide. The powder was then heat-treated at a temperature of  $700^\circ\text{C}$  for approximately 10 hours in a state where dry air was blown on the powder, thereby completing the production of the active material for positive electrodes used in lithium secondary batteries-700 for about 10 hours in a stream of dry air, thereby producing of a positive active material.  
30

Using the positive electrode active material manufactured as in the above, a coin-cell type half-cell active material, a coin-type half-cell was manufactured according to the method used in Example 1.

(Example 14)

LiCoO<sub>2</sub> powder (NC-5 produced by Nippon Chemical of Japan) was dipped in Mg-methoxide sol for approximately 10 minutes, then removed from the sol solution. A commercial LiCoO<sub>2</sub> powder having average particle diameter of 5 was dipped in a Mg-methoxide suspension for about 10 minutes and the coated LiCoO<sub>2</sub> powder was then separated from the suspension. This powder was then dried in an oven set to 120°C for approximately 120 for about 5 hours, thereby producing LiCoO<sub>2</sub> powder coated with Mg-methoxide. The LiCoO<sub>2</sub> powder coated with Mg-methoxide subsequently was heat-treated for approximately 10 hours at 600°C in a state where dry air was blown on the powder to produce active material for a positive electrode used in lithium-ion batteries. Mg-methoxide coated LiCoO<sub>2</sub> powder was subsequently heat-treated for about 10 hours at 600 in a stream of dry air to produce a positive active material.

(Example 15)

LiCoO<sub>2</sub> powder (NC-5 produced by Nippon Chemical of Japan) was dipped in Al-isopropoxide sol for approximately 10 minutes, then removed from the sol solution. A commercial LiCoO<sub>2</sub> powder having average particle diameter of 5 was dipped in an Al-isopropoxide suspension for about 10 minutes, and the coated LiCoO<sub>2</sub> powder was then separated from the suspension. This powder was then dried in an oven set to 120°C for approximately 120 for about 5 hours, thereby producing LiCoO<sub>2</sub> powder coated with Mg-methoxide. The LiCoO<sub>2</sub> powder coated with Al-isopropoxide subsequently was heat-treated for approximately 10 hours at 600°C in a state where dry air was blown on the powder to produce active material for a positive electrode used in lithium-ion batteries. Al-isopropoxide. The Al-isopropoxide LiCoO<sub>2</sub> powder was subsequently heat-treated for about 10 hours at 600 in a stream of dry air to produce a positive active material.

(Example 16)

LiCoO<sub>2</sub> powder (NC-10 produced by Nippon Chemical of Japan) was

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dipped in Mg-methoxide sol for approximately 10 minutes, then removed from the sol solution. A commercial LiCoO<sub>2</sub> powder having average particle diameter of 10 was dipped in a Mg-methoxide suspension for about 10 minutes and then separated from the suspension. This powder was then dried in an oven set to 120°C for approximately at 120 for about 5 hours, thereby producing LiCoO<sub>2</sub> powder coated with Mg-methoxide. The LiCoO<sub>2</sub> powder coated with Mg-methoxide subsequently was heat-treated for approximately 10 hours at 600°C in a state where dry air was blown on the powder to produce active material for a positive electrode used in lithium-ion batteries.

Mg-methoxide LiCoO<sub>2</sub> powder was subsequently heat-treated for about 10 hours at 600 in a stream of dry air to produce a positive active material.

The active material manufactured as in the above, conductive material positive active material, a conductive agent (carbon, product name: Super P), a binder (polyvinylidene fluoride, product name: KF-1300) and a solvent (N-methyl pyrrolidone) were mixed to produce ana positive active material composite slurry for a positive electrode slurry. The slurry was then cast into a tape on an Al foil to shape to manufacture prepare a positive electrode.

Using this the positive electrode; a negative electrode of MCF (meso carbon made from MCF (meso-carbon fiber) material; an organic electrolyte including 1M of LiPF<sub>6</sub> in a mixture of ethylene carbonate, dimethyl carbonate and diethyl carbonate at in a 3:3:1 volume ratio; and the Ashai separator made of polypropylene, a 18650a sheet of microporous polypropylene separator (Ashai Company), a 18650-size cylindrical battery cell having a capacity of 1650mAh was manufactured. Battery life fabricated. The cycle-life characteristics of this battery cell were then measured by setting a 1C capacity to 1650mAh and in a range between 2.75 and at 1C rate in the voltage range of 2.75 to 4.2V.

(Example 17)

LiCoO<sub>2</sub> powder (NC-5 produced by Nippon Chemical of Japan) having average particle diameter of 5 was dipped in an Al-isopropoxide sol for approximately 10 minutes, then removed from the sol solution suspension for about 10 minutes and then separated from the suspension. This powder was



then dried in an oven set to  $120^{\circ}\text{C}$  for approximately at 120 for about 5 hours, thereby producing  $\text{LiCoO}_2$  powder coated with Al-Al isopropoxide. The  $\text{LiCoO}_2$  powder coated with isopropoxide. The Al-isopropoxide coated  $\text{LiCoO}_2$  powder was subsequently was heat-treated for approximately about 10 hours at  $600^{\circ}\text{C}$  600 in a state where dry air was blown on the powder to produce active material for a positive electrode used in lithium-ion batteries. cell.

Using this active material, a positive electrode and a battery were manufactured cell were fabricated using the same method of as in Example 16.

(Example 18)

$\text{Ni}(\text{OH})_2$  (Tanaka Co. of Japan) and  $\text{Co}(\text{OH})_2$  (Kojyundo Chemical of Japan) were mixed to an equivalent ratio of 0.8/0.2 and dispersed in water, after which the mixture underwent an attritor-milling process for approximately 60 minutes at 450 rpm to uniformly mix the mixture. Next, after drying the mixed powder dispersed in water in a drying oven at  $120^{\circ}\text{C}$  for approximately 24 hours, the resulting dry mixture was evenly ground, thereby producing  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$ .  $\text{LiOH}$  (Junsei Co. of Japan) was added to the  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$  to provide 1 equivalent weight of lithium, and ethanol was added to accelerate a reaction between the  $\text{LiOH}$  and  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$ , after which the mixture underwent mortar grinder mixing until almost all the ethanol was no longer present in the mixture (i.e., until a solvent-free mixture was obtained).

After the above, the fully mixed mixture was placed in an aluminous crucible and heat-treated at  $400^{\circ}\text{C}$  in a state where dry air was blown on the mixture, then again heat-treated for 12 hours at  $750^{\circ}\text{C}$ . In both the heat-treating processes, the temperature was raised at a rate of  $3^{\circ}\text{C}/\text{min.}$ , and after reaching the target temperatures ( $400^{\circ}\text{C}$  and  $750^{\circ}\text{C}$ ) and maintaining this state for a predetermined time, the mixture was naturally cooled to produce a  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder.

The  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder produced as in the above was then dipped in Mg-methoxide sol for approximately 10 minutes, then removed from the sol solution. Subsequently, the powder was dried in an oven set at  $120^{\circ}\text{C}$  for approximately 5 hours, thereby producing  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder coated with the Mg-methoxide. The powder was then heat-treated at a temperature of  $500^{\circ}\text{C}$  for approximately 10 hours in a state where dry air was blown on the powder, thereby completing the production of the active material for positive

electrodes used in lithium secondary batteries.

— The active material manufactured as in the above, conductive material (carbon, product name: Super P), a binder (polyvinylidene fluoride, product name: KF-1300) and a solvent (N-methyl pyrrolidone) were mixed to produce an active material composite slurry for a positive electrode. The slurry was then east into a tape shape to manufacture a positive electrode.

— Using this positive electrode, a negative electrode of MCF (meso carbon fiber) material, an organic electrolyte including 1M of  $\text{LiPF}_6$  in a mixture of ethylene carbonate, dimethyl carbonate and diethyl carbonate at a 3:3:1 volume ratio, and the Ashai separator made of polypropylene, a 18650 cylindrical battery having a capacity of 1650mAh was manufactured. Battery life characteristics of this battery were then measured by setting a 1C capacity to 1650mAh and in a range between 2.75 and 4.2V, and  $\text{Co}(\text{OH})_2$  were mixed in an equivalence ratio of 0.8:0.2 and dispersed in water. The mixture was mixed well by milling with an attritor for about 60 minutes at 450 rpm. The mixed powder was dried in a drying oven at 120 °C for about 24 hours and the resulting dried mixture was evenly ground, thereby producing  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$ . LiOH was added to the  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$  to make 1 equivalent of lithium per formula weight of the hydroxide, and ethanol was added to facilitate the reaction between the LiOH and  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$ . The mixture was mixed in a mortar until liquid ethanol disappeared from the mixture.

— Thereafter, the mixed mixture was placed in an alumina crucible and heat-treated at 400 °C in a stream of dry air, then heat-treated again for 12 hours at 750 °C. In both the heat-treating processes, the temperature was raised at a rate of 3 °C/min. The mixture was allowed to stand at the first and the second heat-treating temperatures for predetermined period of time, and the mixture was slowly cooled to produce a  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder.

— The  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder was then dipped in a Mg-methoxide suspension for about 10 minutes, and then separated from the suspension. Subsequently, the powder was dried in an oven at 120 °C for about 5 hours, thereby producing  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder coated with the Mg-methoxide. The powder was then heat-treated at a temperature of 500 °C for approximately 10 hours in a stream of dry air, thereby producing a positive active material.

The positive active material, a conductive agent (carbon, product name: Super P), a binder (polyvinylidene fluoride, product name: KF-1300) and a solvent (N-methyl pyrrolidone) were mixed to produce a positive active material slurry. The slurry was then cast into a tape on an Al foil to prepare a positive electrode.

Using this positive electrode, a negative electrode made from MCF (meso-carbon fiber) material, an organic electrolyte including 1M LiPF<sub>6</sub> in a mixture of ethylene carbonate, dimethyl carbonate and diethyl carbonate in a 3:3:1 volume ratio, and a sheet of microporous polypropylene separator (Ashai Company), a 18650-size cylindrical cell having a capacity of 1650mAh was fabricated. The cycle-life characteristics of this cell were then measured at 1C rate in the voltage range of 2.75 to 4.2V.

(Example 19)

A coin-type half-cell was fabricated by the same procedure as in Example 8 except that LiNi<sub>0.9</sub>Co<sub>0.1</sub>O<sub>2</sub> was coated with an Al-isopropoxide suspension.

(Example 20)

A coin-type half-cell was fabricated by the same procedure as in Example 9 except that an Al-isopropoxide suspension was used instead of the Mg-methoxide suspension.

(Example 21)

A coin-type half-cell was fabricated by the same procedure as in Example 10 except that an Al-isopropoxide suspension was used instead of the Mg-methoxide suspension.

(Example 22)

A coin-type half-cell was fabricated by the same procedure as in Example 14 except that an Al-isopropoxide suspension was used instead of the Mg-methoxide suspension.

(Example 23)

A coin-type half-cell was fabricated by the same procedure as in Example 16 except that an Al-isopropoxide suspension was used instead of the Mg-methoxide suspension.

(Comparative Example 1)

Except for skipping the steps A coin-type half-cell was fabricated by the

same procedure as in Example 1 except that the step of coating the semi-crystalline  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder with the Mg-methoxide sol then heat-treating the coated powder, the same method as that used in Example 1 was used to manufacture positive electrode active material and a coin cell type half cell suspension was omitted.

(Comparative Example 2)

Except for skipping the steps A coin-type half-cell was fabricated by the same procedure as in Example 2 except that the step of coating the semi-crystalline  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder with the Mg-methoxide sol then heat-treating the coated powder, the same method as that used in Example 2 was used to manufacture positive electrode active material and a coin cell type half cell suspension was omitted.

(Comparative Example 3)

Except for skipping the steps A coin-type half-cell was fabricated by the same procedure as in Example 5 except that the step of coating the semi-crystalline  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder with the Mg-methoxide sol then heat-treating the coated powder, the same method as that used in Example 2 was used to manufacture positive electrode active material and a coin cell type half cell suspension was omitted.

(Comparative Example 4)

$\text{Ni}(\text{OH})_2$  (Tanaka Co. of Japan),  $\text{Co}(\text{OH})_2$  (Kojundo Chemical of Japan),  $\text{Ni}(\text{OH})_2$ ,  $\text{Co}(\text{OH})_2$ , and  $\text{Mg}(\text{OH})_2$  were mixed to an equivalent ratio of 0.8:0.15:0.05 and dispersed in water, after which the mixture underwent an attritor milling process for approximately 60 minutes at 450 rpm to uniformly mix the mixture. Next, after drying the mixed powder dispersed in water in a drying oven at  $120^\circ\text{C}$  for approximately 24 hours in an equivalence ratio of 0.8:0.15:0.05 and dispersed in water. The resulting mixture was mixed well by milling with an attritor for about 60 minutes at 450 rpm. The mixed powder was dried in a drying oven at  $120^\circ\text{C}$  for about 24 hours and the resulting dry mixture was evenly ground, thereby producing  $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Mg}_{0.05}(\text{OH})_2$ .  $\text{LiOH}$  (Junsei Co. of Japan) was added to the  $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Mg}_{0.05}(\text{OH})_2$  to provide make 1 equivalent of lithium per formula weight of lithium, the hydroxide, and ethanol was added to accelerate facilitate a reaction between the  $\text{LiOH}$  and  $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Mg}_{0.05}(\text{OH})_2$ , after which the mixture underwent mortar grinder mixing until almost all the

ethanol was no longer present in the mixture (i.e., until the mixture was solvent-free). Next, the fully mixed  $\text{Ni}_{0.8}\text{Co}_{0.15}\text{Mg}_{0.05}(\text{OH})_2$ . The mixture was mixed in a mortar until liquid ethanol disappeared from the mixture. The mixed mixture was placed in an aluminous alumina crucible and heat-treated at  $400^\circ\text{C}$  in a state where dry air was blown on the mixture, then again heat-treated for 12 hours at  $750^\circ\text{C}$  to produce active material for a positive electrode used in lithium-ion batteries. 400 in a stream of dry air, then heat-treated again for 12 hours at  $750^\circ\text{C}$  to produce a positive active material.

Using the positive electrode active material manufactured as in the above, a coin-cell type half-cell was manufactured active material, a coin-type half-cell was fabricated according to the method used in Example 1.

(Comparative Example 5)

Except for skipping the steps of coating the crystalline  $\text{LiCoO}_2$  powder with Mg-methoxide sol then heat treating the coated powder, the same method as that used in Example 9 was used to manufacture positive electrode active material and a coin-cell type half-cell.

A coin-type half-cell was fabricated by the same procedure as in Example 9 except that the step of coating the semi-crystalline  $\text{LiCoO}_2$  powder with the Mg-methoxide suspension was omitted.

(Comparative Example 6)

Except for skipping the steps A coin-type half-cell was fabricated by the same procedure as in Example 11 except that the step of coating the semi-crystalline  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder with the Mg-methoxide sol then heat treating the coated powder, the same method as that used in Example 11 was used to manufacture positive electrode active material and a coin-cell type half cell suspension was omitted.

(Comparative Example 7)

Except for skipping the steps of coating the crystalline  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder with Mg-methoxide sol then heat treating the coated powder, the same method as that used in Example 12 was used to manufacture positive electrode active material and a coin-cell type half-cell. A coin-type half-cell was fabricated by the same procedure as in Example 12 except that the step of coating the semi-crystalline  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  powder with the Mg-methoxide suspension was omitted.

(Comparative Example 8)

Except for skipping the steps of coating the crystalline  $\text{LiNi}_{0.9}\text{Co}_{0.098}\text{Sr}_{0.002}\text{O}_2$  powder with Mg-methoxide sol then heat-treating the coated powder, the same method as that used in Example 13 was used to manufacture positive electrode active material and a coin-cell type half-cell. A coin-type half-cell was fabricated by the same procedure as in Example 13 except that the step of coating the semi-crystalline  $\text{LiNi}_{0.9}\text{Co}_{0.098}\text{Sr}_{0.002}\text{O}_2$  powder with the Mg-methoxide suspension was omitted.

(Comparative Example 9)

$\text{LiCoO}_2$  powder (NC-5 of Nippon-Chemical) was used as is for positive electrode having average particle diameter of 5 was used as a positive active material in a lithium-ion battery for a coin-type half-cell.

(Comparative Example 10)

Except for skipping the step of processing the  $\text{LiCoO}_2$  powder (NC-10 of Nippon-Chemical) using Mg-methoxide sol such that the powder is used as is for positive electrode active material, the same method as that used in Example 16 was used. A coin-type half-cell was fabricated by the same procedure as in Example 16 except that the step of coating the semi-crystalline  $\text{LiCoO}_2$  powder with the Mg-methoxide suspension was omitted.

(Comparative Example 11)

A battery cell as disclosed in the Matsushita Technical Journal Vol. 44, August 1998, pp. 407-412 was used for Comparative Example 11.

(Comparative Example 12)

Except for skipping the steps, a 18650-size cylindrical cell was fabricated by the same procedure as in Example 18 except that the step of coating the semi-crystalline  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder with Mg-methoxide sol and heat-treating the powder, the same method as that used in Example 17 was used to manufacture positive electrode active material and a 18650-type battery. the Mg-methoxide suspension was omitted.

(Comparative Example 13)

A coin-type half-cell was fabricated by the same procedure as in Example 19 except the step of coating the semi-crystalline  $\text{LiNi}_{0.9}\text{Co}_{0.1}\text{O}_2$  powder with the Al-isopropoxide suspension was omitted.

(Comparative Example 14)

LiCoO<sub>2</sub> was mixed a commercial Al<sub>2</sub>O<sub>3</sub>. Using the resulting mixture, a coin-type half-cell was fabricated by the same procedure as in Comparative example 1.

(Comparative Example 15)

LiCoO<sub>2</sub> powder was intimately mixed by grinding with about 1% by weight of Al<sub>2</sub>O<sub>3</sub> and the mixture was then briefly heated at about 800 °C for 1 hour to positive active material. Using the resulting positive active material, a coin-type coin-cell was fabricated by the same procedure as in Comparative example 1.

FIGs. 1A and 1B show SEM pictures, enlarged 1A and 1B show SEM pictures, respectively 200-times and 20,000-times, of the 20,000-times expanded view of the positive active material manufactured according to Example 1 of the present invention; and FIGs. 2A and 2B show SEM pictures, enlarged respectively 300-times and 20,000-times, of the 20,000-times expanded view of the positive active material manufactured according to Comparative Example 1 of the present invention. As can be seen in FIGs. 1A and 2A, the positive active material manufactured according to Example 1 is comprised of clumps that are less than 400 μm in size, whereas the positive active material manufactured according to Comparative Example 1 is comprised of clumps that are greater than 400 μm in size. Further, as shown in FIG. 1B, the positive active material manufactured according to Example 1 is comprised of ultra-fine particles of 0.1 to 0.2 μm in size which aggregate mass together to form small particles of 0.5 to 1 μm in size. On the other hand, as shown in FIG. 2B, the positive active material manufactured according to Comparative Example 1 is comprised of particles that are 1 μm and larger in size that mass greater than 1 μm in size which aggregate together into clumps.

FIG. 3 shows a graph of XRD patterns of the positive active material according to Example 2 and Comparative Example 2 of the present invention. As shown in the drawing, an XRD pattern (a in the drawing) FIG. 3) of the semi-crystalline LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> powder produced by mixing LiOH and Ni<sub>0.8</sub>Co<sub>0.2</sub>(OH)<sub>2</sub> in the acetone solvent of the LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> powder produced by mixing LiOH

and  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$  in the acetone solvent then heat-treated at a temperature of 500°C followed by heat-treating at a temperature of 500 for the first heat-treatment step only is broad and has peaks that are not significantly high, indicative of a semi-crystalline state. Further, if the active material coated with Mg-methoxide undergoes the second heat-treating process as in Example 2, peaks of an XRD pattern of this an XRD pattern (b in FIG. 3) of the  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  powder produced by mixing LiOH and  $\text{Ni}_{0.8}\text{Co}_{0.2}(\text{OH})_2$  in the acetone solvent then heat-treating at a temperature of 500 for the first heat-treatment step and heat-treating at a temperature of 750 for the second heat-treatment step has sharp peaks, which indicates a complete crystalline active material (b in the drawing) are distinct and sharp, indicative of a fully-crystallized state. This XRD pattern is substantially identical to an XRD pattern (c in the drawing) FIG. 3) of the crystalline positive active material of Comparative Example 2 in which Mg is not added. Accordingly, since the coated. Since the XRD pattern of the positive active material of Example 2 is able to maintain the structure (b in FIG. 3) is identical to that of the active material in which Mg is not added, this indicates coated (c in FIG. 3), the results indicate that the Mg-oxide does not permeate/penetrate into the crystalline structure of the positive active material, but, rather, only coats at the surface of the crystalline structure. In FIG. 2-3, " \* " indicates Si standard reference peaks.

FIG. 4 shows a graph of charge and discharge cycle-life characteristics of coin-type batteries manufactured/cells prepared according to Example 1 (a in the drawing), FIG. 4), Example 3 (b in the drawing) FIG. 4) and Comparative Example 1 (c in the drawing). A capacity and a battery life of each of the batteries were measured by FIG. 4). A capacity and a cycle life of each of the cells were measured by charging-discharging the cells in the voltage charging/discharging the batteries, between 2.8V and 4.3V, to 0.1C for 1 cycle, 0.2C for 3 cycles, 0.5C for 10 cycles, and 1C for 85 cycles. range of 2.8V to 4.3V, at 0.1C (1 cycle), 0.2C (3 cycles), 0.5C (10 cycles), and 1C (85 cycles) rates. As shown in FIG. 4, when charge and discharge at a high rate of 1C charge and 1C discharge, the capacity of the battery using the active material of cell according to Example 1 reduced from 72.8mAh/g to 66.8mAh/g 72.8



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mAh/g to 66.8 mAh/g (approximately 8%) after 85 cycles; and the capacity of the battery using the active material of cell according to Example 3 reduced from 122 mAh/g to 77.5mAh/g (approximately 36%) after 85 cycles; and cycles. On the other hand, the capacity of the battery using the active material of cell according to Comparative Example 1 reduced from 111.9mAh/g to 42.6mAh/g 111.9 mAh/g to 42.6 mAh/g (approximately 60%) after 85 cycles. Accordingly, it can be known that, compared to the battery using the prior active material, the battery utilizing the active material of the present invention is stable, has a limited amount capacity reduction and displays exceptional battery life. In summary, characteristics at a high rate of charge and discharge, the results indicate that the positive active materials of Examples 1 and 3 are more stable in high-rate cycling, therefore improved cycle-life over that of Comparative Example 1.

FIGs. 5a and 5b 5A and 5B show SEM pictures of the positive active material powder according to Example 5 and Comparative Example 3, respectively. As shown in the drawing, FIGs. 5A and 5B, the surface of the active material of Example 5 is formed differently apparently different from the surface of the active material of Comparative Example 3 as a result of the coating of the metal oxide over the active material of Example 5 metal oxide coating on the surface of the active material.

XRD patterns of the active material powder positive active materials of Example 5, Comparative Example 3 and Comparative Example 4 are shown respectively by lines A, B(A), (B) and C(C) of FIG. 6. In FIG. 6, “\*” indicates Si standard reference peaks. In FIG. 6, with regard to lattice parameters, a is 2.876 and c is 14.151 in the case a-axis is 2.876 and c-axis is of A, a is 2.883 and c is 14.150 in the case of B, and a is 2.872 and c is 14.204 in the case of C. As shown in the drawing, a significantly different XRD pattern results for the active material of Example 5 compared to the XRD pattern of the active material of Comparative Example 4 in which Mg is doped within the structure of the active material, while the XRD pattern of the active material of Example 5 is substantially identical to that of the active material of Comparative Example 3 in which Mg is not doped within the structure of the active material. This indicates that the active material of Example 5 maintains the structure of the prior active material in which Mg is not doped within the active material structure while

changing only the surface formation to improve electro-chemical characteristics.

FIG. 7 shows a graph of electro-chemical characteristics of the battery manufactured according to Example 5 and Comparative Example 3 while charge and discharge speeds were changed in a range of 2.8V to 4.3V. In the drawing, line (a) corresponds to Example 5 and line (b) corresponds to Comparative Example 3. As shown in the drawing, although a capacity of the battery of Example 5 reduced from 140mAh/g to 90mAh/g, that of Comparative Example 3 reduced from 140mAh/g to 60mAh/g. This shows that, at a high charge/discharge rate, the battery using the active material of Example 5 displays a minimal amount of reduction in battery capacity when compared to Comparative Example 3.

Referring now to FIG. 8, shown are DSC analysis results of pole plates removed from the batteries manufactured according to Example 9 (b in the drawing) and Comparative Example 5 (a in the drawing), the batteries having been charged to 4.1V one time before dismantling of the batteries. The DSC analysis was conducted to determine thermal stability of the charged positive electrode active material.  $\text{LiCoO}_2$ , for example, comes to have a structure of  $\text{Li}_{1-x}\text{CoO}_2$  ( $0.5 < x < 1$ ) in a charged state. Since active material having this structure is unstable, if the temperature in the battery rises, oxygen combined with metal (i.e., cobalt) becomes separated from the metal. The freed oxygen reacts with the electrolyte in the battery such that it is possible for the battery to explode. Accordingly, an oxygen separation temperature and an amount of heat generation are important factors with regard to the stability of batteries. 14.151 in the case of (a), a-axis is 2.883 and c-axis is 14.150 in the case of (b), and a-axis is 2.872 and c-axis is 14.204 in the case of (c). As shown in FIG. 6, significantly different XRD patterns are shown for the positive active material of Example 5 (A) compared to the XRD patterns of the positive active material of Comparative Example 4 (C) in which Mg is doped within the structure of the active material instead of being coated, whereas the XRD pattern of the active material of Example 5 is substantially identical to that of the active material of Comparative Example 3 (B) in which Mg is neither doped nor coated on the active material. The results indicate that the active material of Example 5 maintains the structure of the original active material which is not coated with

Mg indicating that the Mg stay at the surface without penetrating into the bulk of the material. The results also indicate that the electro-chemical characteristics are improved by the surface coating.

FIG. 7 shows a graph of cycle-life characteristics of the cells according to Example 5 and Comparative Example 3 in the voltage range of 2.8V to 4.3V. In FIG. 7, the curve (a) corresponds to Example 5 and the curve (b) corresponds to Comparative Example 3. As shown in FIG. 7, the capacity of the cell for 1C-rate cycling of Example 5 reduced from 140 mAh/g to 90 mAh/g, while that of Comparative Example 3 reduced from 140 mAh/g to 60 mAh/g, showing that the cell capacity of Example 5 has reduced significantly more than that of Comparative Example 3 in the 1C-rate cycling.

FIG. 8 shows DSC analysis results of the cells according to Example 9 (b in FIG. 8) and Comparative Example 5 (a in FIG. 8). These results were obtained using electrodes from the cells charged at 4.1V. The DSC analysis result illustrates the thermal stability of individual sample cells. After charging the cell, the positive active material is converted from  $\text{LiCoO}_2$  to  $\text{Li}_{1-x}\text{CoO}_2$  ( $0.5 \leq x < 1$ ). The charged active material,  $\text{Li}_{1-x}\text{CoO}_2$ , becomes unstable as temperature is increased releasing oxygen gas due to weakened Co-O bonds, showing an exothermic peak in the DSC curve. The released oxygen may react with the electrolyte in the cell causing the cell to explode in the worst case. Both the peak temperature and the peak size which represent the amount of heat released are a measure of the instability of the charge material of the cell.

As shown in FIG. 8, an oxygen-separation temperature of Comparative Example 5 is roughly  $213^\circ\text{C}$ , while it is approximately  $218^\circ\text{C}$  for Example 9. Therefore, the oxygen-separation temperature for Example 9 is about  $5^\circ\text{C}$  higher than that for Comparative Example 5, and a heat-generation exothermic peak temperature for Comparative Example 5 is about  $213^\circ\text{C}$ , while that for Example 9 is about  $5^\circ\text{C}$  higher (approximately  $218^\circ\text{C}$ ) than that for Comparative Example 5. The amount of heat released (peak size) for Example 9 is about half that of Comparative rate for Example 9 is about half that of Comparative Example 5. Accordingly, with the processing of the surface of  $\text{LiCoO}_2$  powder with metal-alkoxide and the heat-treating of the powder, the

metal oxide is formed on the surface of the  $\text{LiCoO}_2$  such that a crystalline structure of the  $\text{LiCoO}_2$  is stabilized. That is, since the crystalline structure on the surface of the  $\text{LiCoO}_2$  is stabilized, it can be assumed that the combination of the cobalt and oxygen is also stabilized. Further, with the formation of a composite metal oxide layer of cobalt and magnesium on the surface of the  $\text{LiCoO}_2$ , any reaction between the positive electrode active material and the electrolyte is suppressed, thereby reducing the oxidation of the electrolyte.

FIG. 9 shows a graph of battery characteristics during charging and discharging at a level of voltage between 2.75V and 4.1V of the battery according to Example 9 and Comparative Example 5. In the drawing, (a) corresponds to the battery of Example 9, while (b) corresponds to the battery of Comparative Example 5. In the case of Comparative Example 5, during 100 cycles charged and discharged to 1C, the capacity of the battery is reduced from 108mAh/g to 38mAh/g (a reduction of 65%), whereas the capacity of the battery of Example 9 is reduced from 114mAh/g to 70mAh/g (a reduction of 39%). Accordingly, relative to Comparative Example 5, the reduction in capacity is considerably smaller at a high rate of charge/discharge and a cycle life is significantly greater for Example 9.

FIG. 10 shows a graph of battery characteristics during charging and discharging at a level of voltage between 2.75V and 4.2V of the battery according to Example 9 and Comparative Example 5. In the drawing, (a) corresponds to the battery of Example 9 and (b) corresponds to the battery of Modified Example 5. In the case of Comparative Example 5, during 100 cycles charged and discharged to 1C, the capacity of the battery is reduced from 120mAh/g to 15mAh/g (a reduction of 88%), whereas the capacity of the battery of Example 9 is reduced from 129mAh/g to 96mAh/g (a reduction of 26%). Accordingly, relative to Comparative Example 5, the reduction in capacity is considerably smaller at a high rate of charge/discharge and a cycle life is significantly greater for Example 9.

FIG. 11 shows a graph of battery characteristics during charging and discharging at a level of voltage between 2.75V and 4.3V of the battery according to Example 9 and Comparative Example 5. In the drawing, (a) corresponds to the battery of Example 9 and (b) corresponds to the battery of Modified Example 5. Accordingly, relative to Comparative Example 5, the

reduction in capacity is considerably smaller at a high rate of charge/discharge and a cycle life is significantly greater for Example 9.

Referring to FIG. 12, (a) illustrates XRD analysis results of the  $\text{LiCoO}_2$  positive electrode active material manufactured according to Comparative Example 5, (b) illustrates XRD analysis results of a pole plate of the battery of Example 10 after the battery has been charged to 4.2V for 1 cycle, Example 5. It is apparent that the Mg coating on the  $\text{LiCoO}_2$  powder improve the stability of the charged active material,  $\text{Li}_{1-x}\text{CoO}_2$ . This improved stability might be due to the fact that the cobalt-magnesium coating layer may limit the access of the charged positive active material to the electrolyte, thereby reducing the oxidation of the electrolyte.

FIG. 9 shows a graph illustrating cycle-life characteristics during charging and discharging the cells of Example 9 and Comparative Example 5 in the voltage range of 2.75V to 4.1V. In FIG. 9, (a) corresponds to the cell of Example 9, while (b) corresponds to the cell of Comparative Example 5. In the case of Comparative Example 5, during 100 charge-discharge cycles at 1C rate, the capacity of the cell is reduced from 108 mAh/g to 38 mAh/g (a reduction of 65%), whereas the capacity of the cell of Example 9 is reduced from 114mAh/g to 70mAh/g (a reduction of 39%) under similar cycling conditions. Relative to Comparative Example 5, the capacity fading of Example 9 is considerably smaller at a high rate (1C rate), therefore showing improved cycle life.

FIG. 10 shows a graph illustrating cycle-life characteristics during charging and discharging in the voltage range of 2.75V to 4.2V of the cell according to Example 9 and Comparative Example 5. In FIG. 10, the curve (a) corresponds to the cell of Example 9 and the curve (b) corresponds to the cell of Comparative Example 5. In the case of Comparative Example 5, after 100 charge-discharge cycles at 1C rate, the capacity of the cell reduced from 120 mAh/g to 15 mAh/g (a reduction of 88%), whereas the capacity of the cell of Example 9 is reduced from 129 mAh/g to a low of 96 mAh/g (a reduction of only 26%). Accordingly, relative to Comparative Example 5, the capacity fading is considerably smaller at a high rate and cycle life is significantly greater for Example 9.

FIG. 11 shows a graph of cycle-life characteristics during charging and

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discharging in the voltage range of 2.75V to 4.3V of the cells according to Example 9 and Comparative Example 5. In FIG. 11, the curve (a) corresponds to the cell of Example 9 and the curve (b) corresponds to the cell of Comparative Example 5. Accordingly, relative to Comparative Example 5, the capacity fading is considerably smaller at a high rate and cycle life is significantly greater for Example 9.

FIG. 12 illustrates XRD analysis results of the positive active materials according to Example 10 and Comparative Example 5. The curve (a) indicates XRD analysis results of the  $\text{LiCoO}_2$  positive active material according to Comparative Example 5. The curve (b) indicates XRD analysis results of the positive active material according to Example 10 after the cell was charged at 4.2V, and the curve (c) indicates XRD analysis results of the positive active material according to Comparative Example 5 after the cell was charged at 4.2V. As shown in (a) and (c) of FIG. 12, it indicates and (c) illustrates XRD analysis results of a pole plate of the battery of Comparative Example 5 after the battery has been charged one time to 4.2V. As shown in (a) and (c) of the drawing, it can be known that as a result of charging, the structure of  $\text{LiCoO}_2$  changes from a hexagonal structure to a monoclinic structure (reference, J. Electro. Chem. Soc. Vol. 143, No. 3, 1006, p. 1114-1122). On the other hand, the  $\text{LiCoO}_2$  powder of Example 10 maintains its hexagonal structure even after charging, indicative of a stable surface obtained as a result of the coating of the magnesium oxide.

Referring to FIG. 13, (b) in the drawing the curve (b) illustrates DSC analysis results of a pole plate of the battery cell of Example 10 after the battery has been charged one time to 4.2V, and (a) in the drawing cell was charged at 4.2V, and the curve (a) illustrates DSC analysis results of a pole plate of the battery cell of Comparative Example 5 after the battery has been charged one time to cell was charged at 4.2V. As shown in the drawing, a FIG. 13, an exothermic peak temperature of a heat generation reaction caused by the separation of oxygen is  $211^\circ\text{C}$  for the oxygen release is  $211^\circ\text{C}$  for Comparative Example 5, while it is  $227^\circ\text{C}$  for Example 10. Accordingly, Example 10 has a roughly  $16^\circ\text{C}$  about a  $16^\circ\text{C}$  higher oxygen separation release temperature than Comparative Example 5.

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In FIG. 14, the curve (b) illustrates DSC analysis results of a pole-plate of the battery cell of Example 10 after the battery has been charged one time to 4.1V, and (a) in the drawing cell was charged at 4.1V, and the curve (a) illustrates DSC analysis results of a pole-plate of the battery cell of Comparative Example 5 after the battery has been charged one time to cell was charged at 4.1V. As shown in the drawing, a FIG. 14, an exothermic peak temperature of a heat generation reaction caused by the separation of oxygen is 213°C for the oxygen release is 213 for Comparative Example 5, while it is 227°C 227 for Example 10. Accordingly, Example 10 has a roughly 15°C about a 15 higher oxygen separation decomposition temperature than Comparative Example 5, and the heat generation amount amount exothermic heat for Example 10 is about half that of Comparative Example 5.

Referring to FIG. 15, (b) illustrates DSC analysis results of the cell of Example 11 after the cell was charged at 4.1V, and (a) illustrates DSC analysis results of the cell of Comparative Example 6 after the cell was charged at 4.1V. As shown in FIG. 15, the cell according to Comparative Example 6 emits heat of about 20mW at 223, while the cell according to Example 11 emits heat of about 6mW at 232. Accordingly, Example 11 has about a 9 higher oxygen decomposition peak temperature than Comparative Example 6, and the amount of exothermic heat for Example 11 is about one-third that of Comparative Example 6.

Referring to FIG. 16, (b) illustrates DSC analysis results of a pole plate of the battery of Example 11 after the battery has been charged one time to 4.1V, and (a) in the drawing the cell of Example 12 after the cell was charged at 4.3V, and (a) illustrates DSC analysis results of a pole-plate of the battery cell of Comparative Example 6 after the battery has been charged one time to 4.1V. As shown in the drawing, a thermal generation amount of approximately 20mW occurs at 223°C for 7 after the cell was charged at 4.3V. As shown in FIG. 16, the cell of Comparative Example 7 6, and approximately 6mW occurs at 232°C for Example 11 emits exothermic heat of about 15mW at 213, and the cell of Example 12 emits heat of about 10mW at 225. Accordingly, Example 11 has a roughly 9°C 12 has about a 12 higher oxygen separation decomposition peak temperature than Comparative Example 6, and the heat generation amount for

Example 11 is about one-third that of Comparative Example 6-7.

Referring to FIG. 16-17, (b) illustrates DSC analysis results of a pole plate of the battery of Example 12 after the battery has been charged one time to the cell of Example 13 after the cell was charged at 4.3V, and (a) in the drawing illustrates DSC analysis results of a pole plate of the battery cell of Comparative Example 7 after the battery has been8 after the cell was charged at 4.3V. As shown in FIG. 17, the cell according to Comparative charged one time to 4.3V. As shown in the drawing, a thermal generation amount of approximately 15mW occurs at 213°C for Comparative Example 7, and approximately 10mW occurs at 225°C for Example 12. Accordingly, Example 12 has a roughly 12°C higher oxygen separation temperature than Comparative Example 6.

Referring to FIG. 17, a thermal generation amount of approximately 40mW occurs at 217°C for Comparative Example 8, and approximately 2mW occurs at 227°C for Example 13. Example 8 emits exothermic heat of about 10mW at 217, and the cell according to Example 13 emits heat of about 2mW at 227. Accordingly, Example 13 has a roughly 10°C about a 10 higher oxygen separation decomposition peak temperature than Comparative Example 8, and the heat generation amount for amount of exothermic heat of Example 13 is about one-third that of Comparative Example 8.

FIG. 18 shows a TEM (tunnel(transmission electron microscope) picture of active material according to Example 14. Example 14. The LiCoO<sub>2</sub> active material not coated with metal alkoxide sol/Mg-methoxide suspension is a crystalline material having approximately a 5.4μm diameter such that the surface of the material is smooth. However, in the active material of Example 14, which is coated with Mg-alkoxide sol/Mg-methoxide suspension then heat-treated, minute particles of approximately 5-15nm surround a periphery of LiCoO<sub>2</sub>, the particles having been excited by of a composite of cobalt and magnesium, a metal oxide such as magnesium oxide, etc.

FIG. 19 shows a TEM picture of the active material of Example 15. In Example 15, the active material is coated with Al-isopropoxide and heat-treated. As in the drawing, in this active material, a double-layer structure excited by a composite metal oxide of cobalt and aluminum or a metal Al-



isopropoxide and is heat-treated. As shown in FIG. 19, a double layer structure made of a composite metal oxide of cobalt and aluminum or a metal oxide such as oxide such as aluminum oxide is formed on the surface of the particles of  $\text{LiCoO}_2$ . Accordingly, the active material of the present invention coated with metal alkoxide sol on its surface then heat treated clearly has a different form compared to the material that is not processed in this manner.

FIG. 20 shows a graph of a cycle life of the batteries manufactured according to Example 16 and Comparative Example 10. The batteries of Example 16 and Comparative Example 10 underwent formation at a rate of 0.2C, then were charged/discharged to 1C. In FIG. 20, (a) corresponds to Example 16 and (b) corresponds to Comparative Example 10. In comparing battery life characteristics of the batteries over 250 cycles, the capacity of Comparative Example 10 reduced by approximately 30% compared to its initial capacity, while the capacity of Example 16 reduced by approximately 20% compared to its initial capacity. It is therefore known that the cycle life of Example 16 is superior to that of Comparative Example 10.

FIG. 21 shows a graph of charge and discharge characteristics of the battery manufactured according to Example 17. After charging the battery at a rate of 0.5C, a discharge rate of the battery was changed from 0.2C to 0.5C, 1C and 2C to measure battery characteristics. FIG. 22 shows a graph of charge and discharge characteristics of the battery manufactured according to Comparative Example 11. In comparing the charge/discharge characteristics of Example 17 and Comparative Example 11, the characteristics are similar up to 1C, but when reaching 2C, the amount of reduction in capacity for Example 17 is significantly smaller than Comparative Example 11.

FIG. 23 shows graph of cycle life characteristics of the batteries manufactured according to Example 18 (a in the drawing) and Comparative Example 12 (b in the drawing). As shown in FIG. 23, cycle life characteristics for Example 18 are better than that of Comparative Example 12 up to roughly 100 cycles, after which the characteristics are substantially similar.

Although the present invention has been described in detail hereinabove, it should be clearly understood that many variations and/or modifications of the basic inventive concepts herein taught which may appear to those skilled in the present art will still fall within the spirit and scope of the

aluminum oxide is formed on the surface of the particles of  $\text{LiCoO}_2$ . Accordingly, the active material of the present invention coated with metal alkoxide suspension on its surface then heat-treated clearly has a different form compared to the material that is not processed in this manner.

FIG. 20 shows a graph of cycle-life characteristics of the cells according to Example 16 and Comparative Example 10. The cells of Example 16 and Comparative Example 10 had formation cycles at 0.2C rate, and then were charged-discharged at 1C rate. In FIG. 20, (a) corresponds to Example 16 and (b) corresponds to Comparative Example 10. In comparing cycle-life characteristics of the cells over 250 cycles, the capacity of Comparative Example 10 reduced by about 30% compared to its initial capacity, while the capacity of Example 16 reduced by only about 20% compared to its initial capacity. It indicates that the cycle life of Example 16 is superior to that of Comparative Example 10.

FIG. 21 shows a graph of discharge curves of the cell according to Example 17. After charging the cell at 0.5C rate, the discharge rate was varied from 0.2C to 0.5C, 1C, and 2C to measure cell performance at various rates. The cell showed almost full capacity even at 2C rate indicating that it has an excellent rate capability.

FIG. 22 shows a graph of discharge curves of the cell according to Comparative Example 11. In comparing the discharge characteristics of Example 17 of FIG. 21 and Comparative Example 11 of FIG. 22, the characteristics are similar up to 1C rate, but at 2C rate, the amount of reduction in capacity for Example 17 is significantly smaller than Comparative Example 11.

FIG. 23 shows a graph of cycle-life characteristics of the cells according to Example 18 (open circles in the drawing) and Comparative Example 12 (filled circles in the drawing). As shown in FIG. 23, cycle-life characteristics for Example 18 are better than those of Comparative Example 12 up to about 100 cycles, after which the characteristics are substantially similar.

The charge and discharge characteristics of the positive active materials according to Example 19 and Comparative example 13 are presented respectively by lines (B) and (A) of FIG. 24. It was evident from FIG. 24, the  $\text{Al}_2\text{O}_3$  coatings cause to deteriorate capacity and voltage in the Ni-based active

material. The result is believed that Al reacts with the Ni-based active material at the surface of the particle and its structure is modified, thereby deteriorating capacity and voltage. These results indicate that a Ni-based positive active material obtained from Japanese Patent Laid-Open Hei. 9-55210 exhibits low capacity and voltage than a Co-based positive active material of the present invention.

To compare the structure of the synthesized  $\text{Al}_2\text{O}_3$  of the present invention and the commercial  $\text{Al}_2\text{O}_3$  of Comparative example 15, the XRD was measured. The active  $\text{Al}_2\text{O}_3$  was prepared by suspending Al-isopropoxide powder in ethanol for 10 hours, drying the resulting suspension at 100 °C for 24 hours to obtain a white powder and heat-treating the white powder at 600 °C for 10 hours. The resulting  $\text{Al}_2\text{O}_3$  has amorphous and active properties which are different from the commercial  $\text{Al}_2\text{O}_3$  having crystalline and inactive properties. Such a difference is evidently shown in FIG. 25. The line (A) which indicates the XRD result of the inactive  $\text{Al}_2\text{O}_3$  in FIG. 25 teaches that it is crystalline and the line (B) which indicates the XRD result of the active  $\text{Al}_2\text{O}_3$  in FIG. 25 teaches that it is amorphous.

Each of the active  $\text{Al}_2\text{O}_3$  and inactive  $\text{Al}_2\text{O}_3$  was added, respectively, to the mixture of the  $\text{LiCoO}_2$  positive active material, a polyvinylidene fluoride binder, and a carbon conductive agent to prepare positive active material slurries. Using the prepared positive active material slurries, coin-type half-cells were fabricated. The charge and discharge characteristics of the coin-type half-cells were measured and the results are shown in FIG. 26. For reference, the charge and discharge characteristic of the coin-type half-cells containing only  $\text{LiCoO}_2$  (A) was shown in FIG. 26. As shown in FIG. 26, the coin-type half-cell containing the active  $\text{Al}_2\text{O}_3$  and  $\text{LiCoO}_2$  (B) gives higher capacity (about 159 mAh/g) than that containing the inactive  $\text{Al}_2\text{O}_3$  (C) and  $\text{LiCoO}_2$ . These results indicate that the commercial inactive  $\text{Al}_2\text{O}_3$  does not improve the cell performance. It is assumed that the positive active material with the commercial  $\text{Al}_2\text{O}_3$  according to Comparative example 15 (prepared by the procedure in U.S. Patent No. 5,705,291) does not improve cell performance.

The SEM pictures of the positive active materials according to Example 21 and Comparative example 15 are shown in FIGs. 27 and 28, respectively.

As shown in FIG. 28, Al is partially doped into  $\text{LiCoO}_2$  in Comparative example 15. In contrast, Al is coated on the  $\text{LiCoO}_2$  in Example 15. This difference is believed that the Al-isopropoxide solution is used in Example 15 and  $\text{Al}_2\text{O}_3$  powder is used in Comparative example 15.

5 In order to identify the structure of the positive active materials precisely according to Example 21 and Comparative example 15, an EDX analysis was carried out. The results are presented in FIGs. 29 and 30, respectively. It is shown from FIGs. 29 and 30 that the structure of the positive active material according to Example 21 is different from that according to Comparative  
10 example 15.

Although the present invention has been described in detail hereinabove, it should be clearly understood that many variations and/or modifications of the basic inventive concepts taught herein, which may appear to those skilled in the present art, will still fall within the spirit and scope of the  
15 present invention, as defined in the appended claims.

~~present invention, as defined in the appended claims.~~

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## WHAT IS CLAIMED IS:

1. Active material for a positive electrode used in lithium secondary batteries of Formula 1 below, a surface of the active material being coated with metal oxide;

5 [Formula 1]

$\text{LiA}_{1-x-y}\text{B}_x\text{C}_y\text{O}_2$ . A positive active material for a rechargeable lithium battery comprising:

a core comprising at least one compound represented by Formula 1;  
and

10 an active metal oxide shell formed on the core, the metal oxide being capable of stabilizing a structure of the active material;

Formula 1

$\text{LiA}_{1-x-y}\text{B}_x\text{C}_y\text{O}_2$ ,

where  $0 \leq x \leq 0.3$ ,  $0 \leq y \leq 0.04$ , and  $0.01$ ;

15 A is an element selected from the group consisting of Ni, Co and Mn;

B is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al; and

20 C is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al.

-Al.

2. The 2. The positive active material of claim 1 wherein a metal in the active metal oxide shell is an element selected from the group consisting of Mg, Al, Co, K, Na and Ca.

25 3. The positive active material of claim 2 wherein the metal in the active metal oxide shell is Al.

4. The positive active material of claim 1 wherein the active metal oxide has an amorphous phase.

30 5. The 5. The positive active material of claim 1 wherein the positive electrode active material is formed by of minute particles in an agglomerated state such that a particle size of the active material is between 0.1 and  $400\mu\text{m}$ -100.

4. The 6. The positive active material of claim 1 wherein the

positive electrode active material is  $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ , where  $0 < x \leq 0.3$ ,  
—  $\text{LiCoO}_2$ .

5 5. The positive active material of claim 1 wherein the active material comprises at least one of the A, B and C metals, and a Mg composite metal oxide, and a surface of the active material oxide shell is processed with minute particles of 5-15nm in size.

6. The active material of claim 1 wherein the active material comprises at least one of the A, B and C metals, and a double layer structure of a Al composite metal oxide processed on a surface of the active material.

10 — 7. A method of manufacturing an active material for a positive electrode used in lithium secondary batteries of Formula 1 below, the method comprising the steps of:

— producing a crystalline powder or a semi-crystalline powder of Formula 1;

15 — coating the crystalline powder or the semi-crystalline powder with metal alkoxide sol; and

— heat treating the powder coated with the metal alkoxide sol;

— [Formula 1]

—  $\text{LiA}_{1-x}\text{B}_x\text{C}_y\text{O}_2$

20 — where  $0 < x \leq 0.3$ ,  $0 \leq y \leq 0.01$ , and

— A is an element selected from the group consisting of Ni, Co and Mn;

— B is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al; and

25 — C is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al.

— 8. The method of claim 7 wherein the metal alkoxide is selected from the group consisting of Mg, Al, Co, K, Na and Ca.

— 9. The method of claim 8 wherein the metal alkoxide is Mg alkoxide.

30 — 10. The method of claim 7 wherein a concentration of metal in the metal alkoxide 1-10% by weight of alcohol.

— 11. The method of claim 7 wherein the heat treating process is performed at a temperature between 400 and 900°C.

— 12. The method of claim 7 wherein in the step of manufacturing the crystalline or semi-crystalline powder further comprises the steps of:

\_\_\_\_\_ mixing an A metal salt, a B metal salt and a C metal salt with a solvent to form a  $A_{1-x-y}B_xC_y(OH)_2$  precursor material;

\_\_\_\_\_ adding then mixing lithium salt and a solvent to the precursor material to form a mixture; and

5 \_\_\_\_\_ heat-treating the mixture.

\_\_\_\_\_ 13. The method of claim 12 wherein in the case where the powder is a crystalline powder, the heat treating step includes a first heat-treating process conducted at a temperature between 400 and 550°C and a second heat-treating process conducted at a temperature between 700 and 900°C.

10 \_\_\_\_\_ 14. The method of claim 13 wherein in the case where the powder is a semi-crystalline powder, the heat-treating step is conducted at a temperature between 400 and 600°C.

\_\_\_\_\_ 15. The method of claim 7 wherein the positive electrode active material is  $LiNi_{1-x}Co_xO_2$ , where  $0 < x \leq 0.3$ .

15 \_\_\_\_\_ 16. A lithium secondary battery using active material for a positive electrode of Formula 1 below, a surface of the active material being coated with metal oxide,

\_\_\_\_\_ [Formula 1]

\_\_\_\_\_  $LiA_{1-x-y}B_xC_yO_2$

20 \_\_\_\_\_ where  $0 < x \leq 0.3$ ,  $0 \leq y \leq 0.01$ , and

\_\_\_\_\_ A is an element selected from the group consisting of Ni, Co and Mn;

\_\_\_\_\_ B is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al; and 8. \_\_\_\_\_

25 \_\_\_\_\_ A rechargeable lithium battery comprising a positive active material, the positive active material comprising a core comprising at least one compound represented by Formula 1 and an active metal oxide shell formed on the core, the active metal oxide being capable of stabilizing a structure of the active materials.

\_\_\_\_\_ Formula 1

\_\_\_\_\_  $LiA_{1-x-y}B_xC_yO_2$ ,

30 \_\_\_\_\_ where  $0 < x < 0.3$ ,  $0 < y < 0.01$ ;

\_\_\_\_\_ A is an element selected from the group consisting of Co and Mn;

\_\_\_\_\_ B is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al; and

\_\_\_\_\_ C is an element selected from the group consisting of Ni, Co, Mn, B,

Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al.

9. The rechargeable lithium battery of claim 8 wherein the metal in the active metal oxide shell is an element selected from the group consisting of Mg, Al, Co, K, Na and Ca.

10. The rechargeable lithium battery of claim 9 wherein a metal in the active metal oxide shell is Al.

11. The rechargeable lithium battery of claim 8 wherein the active metal oxide has an amorphous phase.

12. A positive active material for a rechargeable lithium battery comprising:

a core comprising  $\text{LiCoO}_2$ ; and

an active metal oxide shell formed on the core.

13. The positive active material of claim 12 wherein a metal in the active metal oxide shell is an element selected from the group consisting of Mg, Al, Co, K, Na and Ca.

14. The positive active material of claim 13 wherein the metal in the active metal oxide shell is Al.

15. The positive active material of claim 12 wherein the active metal oxide has an amorphous phase.

16. The positive active material of claim 12 wherein the positive active material is formed of minute particles in an agglomerated state such that a particle size of the active material is between 0.1 and 100 .

17. The positive active material of claim 12 wherein the active metal oxide shell is processed with minute particles of 5-15nm in size.

18. A positive active material for a rechargeable lithium battery prepared by producing a crystalline powder or a semi-crystalline powder of Formula 1:

coating the crystalline powder or the semi-crystalline powder with a metal alkoxide suspension; and

heat-treating the coated powder.

the positive active material comprising a core and an active metal oxide shell formed on the core, the metal oxide being capable of stabilizing the structure of the active material:

Formula 1



$\text{LiA}_{1-x}\text{B}_x\text{C}_y\text{O}_2$ ,

where  $0 < x < 0.3$ ,  $0 < y < 0.01$ ;

A is an element selected from the group consisting of Co and Mn;

B is an element selected from the group consisting of Ni, Co, Mn, B,  
5 Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al; and

C is an element selected from the group consisting of Ni, Co, Mn, B,  
Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al.

19. The positive active material of claim 18 wherein a metal in the  
active metal oxide shell is an element selected from the group consisting of Mg,  
10 Al, Co, K, Na and Ca.

20. The positive active material of claim 19 wherein the metal in the  
active metal oxide shell is Al.

21. The positive active material of claim 18 wherein the active metal  
oxide has an amorphous phase.

22. The positive active material of claim 18 wherein the positive  
active material is formed of minute particles in an agglomerated state such that  
a particle size of the active material is between 0.1 and 100 .

23. The positive active material of claim 18 wherein the active metal  
oxide shell is processed with minute particles of 5-15nm in size.

24. A positive active material for a rechargeable lithium battery  
comprising:

a core comprising  $\text{LiCoO}_2$ ; and

an active  $\text{Al}_2\text{O}_3$  shell formed on the core.

25. The positive active material for a rechargeable lithium battery of  
claim 24 wherein the active  $\text{Al}_2\text{O}_3$  has an amorphous phase.

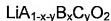
26. The positive active material for a rechargeable lithium battery of  
claim 24 wherein the positive active material is formed of minute particles in an  
agglomerated state such that a particle size of the active material is between  
0.1 and 100 .

30. The positive active material of claim 24 wherein the active  $\text{Al}_2\text{O}_3$   
shell is processed with minute particles of 5-15nm in size.

## ABSTRACT OF THE DISCLOSURE

Disclosed is a positive active material for a positive electrode used in lithium secondary batteries of Formula 1 below and a method manufacturing the same, a surface of the active material being coated with metal oxide. The method includes the steps of producing a crystalline powder or a semi-rechargeable lithium battery. The positive active material includes a core including at least one compound represented by Formula 1 and an active metal oxide shell formed on the core. Formula 1  
crystalline powder of Formula 1; coating the crystalline powder or the semi-crystalline powder with metal alkoxide sol; and heat treating the powder coated with the metal alkoxide sol.

[Formula 1]



where  $0 \leq x \leq 0.3$ ,  $0 \leq y \leq 0.01$ , and

A is an element selected from the group consisting of Ni, Co and Mn;  
Mn; B is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al; and  
and C is an element selected from the group consisting of Ni, Co, Mn, B, Mg, Ca, Sr, Ba, Ti, V, Cr, Fe, Cu and Al.